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THERMODYNAMICS

& Chemical equilibria

Mathematics Involved in Chemical Thermodynamics

Differential Formulas:

(1) $\frac{d(c)}{dx} = 0$

(2) $\frac{d(x^n)}{dx} = nx^{n-1}$

(3) $\frac{d(cx^n)}{dx} = c\frac{d(x^n)}{dx} = cnx^{(n-1)}$

(4) $\frac{d(\sin x)}{dx} = \cos x$

(5) $\frac{d(\cos x)}{dx} = -\sin x$

(6) $\frac{d(a^x)}{dx} = a^x \, lna$

(7) $\frac{d(e^x)}{dx} = e^x$

(8) $\frac{d(\ln x)}{dx} = \frac{1}{x}, x > 0$

(9) $\frac{d[f(x)g(x)]}{dx} = f(x)\frac{d[g(x)]}{dx} + g(x)\frac{d[f(x)]}{dx}$

(10) $\frac{d}{dx}\left[\frac{f(x)}{g(x)}\right] = \frac{g(x)\frac{d[f(x)]}{dx} - f(x)\frac{d[g(x)]}{dx}}{[g(x)]^2}$

Integration Formulas:

(1) $\int dx = x + c, \; \int dt = t + c$

(2) $\int x^n dx = \frac{x^{n+1}}{n+1} + c$

(3) $\int kx^n dx = k\int x^n dx = k\frac{x^{n+1}}{(n+1)} + c$

(4) $\int e^x dx = e^x + c$

(5) $\int \frac{1}{x} dx = \ell n_e x + c$

(6) $\int \sin x\, dx = -\cos x + c$

(7) $\int \cos dx = \sin x + c$

(8) $\int [f(x)g(x)]dx = f(x)\int g(x)dx - \int\left[\frac{d}{dx}f(x).\int g(x)dx\right]dx$

Logarithms:

$\log_{10} 2 = 0.3010$; $\log_{10} 3 = 0.4771$; $\log_{10} 5 = 0.699$; $\log_{10} 7 = 0.8451$

$$\boxed{\ln 2 = 2.303 \times \log_{10} 2 = 2.303 \times 0.3010 = 0.6932}$$

$$\boxed{\log_{10} x^m = m\log_{10} x}; \quad \boxed{\log\frac{m}{n} = \log m - \log n}; \quad \boxed{\log(m \times n) = \log m + \log n}$$

$$\Rightarrow \quad \boxed{\log_{10} x = -2 \Rightarrow x = 10^{-2} = \frac{1}{100} = 0.01}$$

$$\Rightarrow \quad \boxed{\log_{10}^{10} = 1} \quad \Rightarrow \quad \boxed{\log_{10}(a/b) = \log_{10} a - \log_{10} b}$$

Important Conversion Factors

1. $1\ \text{cal} = 4.184\text{J} = 4.184 \times 10^7\ \text{erg}$
2. $\text{Newton} = 10^5\ \text{atm cm}^3$
3. $\text{Joule} = 10^7\ \text{ergs} = 0.239\ \text{cal}$
4. Electron Volt, $\text{eV} = 1.6021 \times 10^{12}\ \text{erg molecule}^{-1}$

   $= 1.6021 \times 10^{-19}\ \text{J molecule}^{-1}$

   $= 96.48\ \text{kJ mol}^{-1} = 23.06\ \text{kcal mol}^{-1}$

   $= 8065.5\ \text{cm}^{-1}$
5. $1\ \text{atm} = 760\ \text{mm Hg} = 760\ \text{Torr} = 101325\ \text{N M}^{-2} = 101.325\ \text{kPa}$
6. $1\ \text{mm Hg} = 1\ \text{torr} = 133.322\ \text{N M}^{-2}$
7. $1\ \text{a.m.u.} = 1.66 \times 10^{-24}\ \text{g} = 1.66 \times 10^{-27}\ \text{kg} \equiv 931.5\ \text{MeV}$
8. $1\ \text{cm}^{-1} = 1.986 \times 10^{-23}\ \text{J} = 1.240 \times 10^{-4}\ \text{eV}$
9. $1\ \text{D} = 3.336 \times 10^{-30}\ \text{cm}$
10. $1\ \text{Å} = 10^{-8}\ \text{cm} = 10^{-10}\ \text{m}$

What is a function?

Function is a rule that relates two or more variable. If $z = 3x + y$ than z is a function of x and y. In ideal gas equation P is a function of T and V, T is a function of P and V, V is a function of T and P.

Operator: That operates the function

Properties of operators:

(1) The square of an operator is defined as the product of the operator with itself. $\hat{A}^2 = \hat{A}\hat{A}$. Let us find the square of the differentiation operator.

$$\hat{D}^2 f(x) = \hat{D}\left(\hat{D}f\right) = \hat{D}f' = f''; \qquad \hat{D}^2 = d^2/dx^2$$

(2) Commutation: The commutator $\left[\hat{A}, \hat{B}\right]$ of the operators $\hat{A}$ and $\hat{B}$ as the operator $\hat{A}\hat{B} - \hat{B}\hat{A}$:

$$\left[\hat{A}, \hat{B}\right] \equiv \hat{A}\hat{B} - \hat{B}\hat{A}$$

If $\hat{A}\hat{B} = \hat{B}\hat{A}$, then $\left[\hat{A}, \hat{B}\right] = 0$, and we say that $\hat{A}$ and $\hat{B}$ commute. If $\hat{A}\hat{B} \neq \hat{B}\hat{A}$, then $\hat{A}$ and $\hat{B}$ do not commute. Note that $\left[\hat{A}, \hat{B}\right]f = \hat{A}\hat{B}f - \hat{B}\hat{A}f$. Since the order in which we apply the operators 3 and d/dx makes no difference, we have

$$\left[\hat{3}, \frac{d}{dx}\right] = \hat{3}\frac{d}{dx} - \frac{d}{dx}\hat{3} = 0$$

Now, $$\left[\frac{d}{dx}, \hat{x}\right] = \hat{D}\hat{x} - \hat{x}\hat{D} = 1$$

The operators d/dx and $\hat{x}$ do not commute.

In calculus (a branch of mathematics) the **derivative** is a measure of how a function changes as its input changes. Loosely speaking, a derivative can be thought of as how much one quantity is changing in response to changes in some other quantity; for example, the derivative of the position of a vehicle with respect to time is the instantaneous velocity at which the vehicle is traveling. The process of finding a derivative is called **differentiation.** The reverse process is called **antidifferentiation**. The fundamental theorem of calculus states that antidifferentiation is the same as integration.

Differentiation is a method to compute the rate at which a dependent output *y* changes with respect to the change in the independent input *x*.

This rate of change is called the **derivative** of *y* with respect to *x*. In more precise language, the dependence of *y* upon *x* means that *y* is a function of *x*. This functional relationship is often denoted $y = f(x)$, where *f* denotes the function. If infinitesimal change in *x* is denoted by *dx*, and the derivative of *y* with respect to *x* is written

dy over dx. $\boxed{\frac{dy}{dx}}$

In **mathematics**, a **partial derivative** of a **function** of several variables is its derivative with respect to one of those variables, with the others held constant as opposed to the total derivative.

For a function of several variables, ~~for example f(x,y,z), the~~ partial derivatives are simply usual derivative in one of the variables when you keep the other variables fixed. For example, take

$$f = 3xy + yz^2$$

In this example f is a function of x,y and z and we can caleulate the value of partial derivative inall form

$$\left(\frac{\partial f}{\partial x}\right)_{y,z};\left(\frac{\partial f}{\partial y}\right)_{x,z};\left(\frac{\partial f}{\partial z}\right)_{x,y}$$

Total derivative is just the usual derivative (with respect to x) of the function f. It can be expressed in terms of partial differentiation as

$$df=\left(\frac{\partial f}{\partial x}\right)_{y,z}dx+\left(\frac{\partial f}{\partial y}\right)_{x,z}dy+\left(\frac{\partial f}{\partial z}\right)_{x,y}dz$$

Cyclic Rule -The **triple product rule**, known variously as the *cyclic chain rule, cyclic relation*, or ***Euler's chain rule***, is a formula which relates **partial derivatives** of three interdependent variables. The rule finds application in **thermodynamics**.

The triple product rule for such interrelated variables *x*, *y*, and *z* comes from using a reciprocity relation is given by

$$\boxed{\left(\frac{\partial x}{\partial y}\right)_z\left(\frac{\partial y}{\partial z}\right)_x\left(\frac{\partial z}{\partial x}\right)_y=-1}$$

This relation may be written in the form of Pressure P, Volume V and Temperature T.

Thermodynamic Coefficient: The degree of expansion divided by the change in temperature at constant pressure is called the material's coefficient of thermal expansion and generally varies with temperature.

$$\alpha=\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

In thermodynamics and fluid mechanics, **compressibility** is a measure of the relative volume change of a fluid or solid as a response to a pressure (or mean stress) change at constant temperature.

$$\beta=-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

Note: most textbooks use the notation κ for this quantity

where *V* is volume and *P* is pressure

The above statement is incomplete, because for any object or system the magnitude of the compressibility depends strongly on whether the process is adiabatic or isothermal. Accordingly **isothermal** compressibility is defined:

$$\beta_T=-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

where the subscript *T* indicates that the partial differential is to be taken at constant temperature

Adiabatic compressibility is defined:

$$\beta_s=-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_s$$

ISOCHORIC THERMAL PRESSURE EXPANSION COEFFICIENT:

$$\gamma = \frac{1}{P}\left(\frac{\partial P}{\partial T}\right)_V$$

State Function: In thermodynamics, a **state function**, *state quantity*, or a *function of state*, is a property of a system that depends only on the current state of the system, not on the way in which the system acquired that state. For example, internal energy, enthalpy and entropy are *state quantities* .In contrast, mechanical work and heat are process quantities .

To prove: State function we use Euler's theorem. This theorem applies on linear equation (Not zig-zag equation according to Euler)

If z is function of x and y variable.

$$z = z(x, y); \quad dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$

Put , $M = \left(\frac{\partial z}{\partial x}\right)_y$, $N = \left(\frac{\partial z}{\partial y}\right)_x$ So, equation change from zig-zag to linear

$$dz = Mdx + Ndy$$

Than for z being a state function it must follow this relation.

Translational entropy of the molecule

$$S_{tr} = \ell n\left(\frac{2\pi mkT}{h^2}\right)^{1/2} \frac{V\, e^{3/2}}{N_A}$$

Where, V = Volume of the system, N_A = Avogadro's number, m = Mass of the molecule
h = Planck's constant; k = Boltzmann's constant, T = absolute temperature (K)

Rotational entropy of the molecule

$$S_{rot} = N\bar{k}\ell n\left[\frac{\pi^{1/2}}{\sigma}\prod_{j=1}^{3}\left(\frac{8\pi^2 I_j kT}{h^2}\right)^{1/2}\right]$$

Where, I_j = Principal moments of inertia of the molecule, σ = Symmetry number of the molecule.
h = Planck's constant, k = Boltzmann's constant, T = absolute temperature (K)

Vibrational entropy of the molecule.

$$S_{vib} = \sum_{j=1}^{\alpha}\left\{\frac{hV_j \exp\left(-hV_j/2kT\right)}{kT\left[1-\exp\left(-hV_j/2kT\right)\right]} - \ell n\left[1-\exp\left(-hV_j/2kT\right)\right]\right\}$$

Where, n_j = Frequencies of normal vibrations in molecule, h = Planck's constant
k = Boltzmann's constant T = Absolute temperature (K)

SYSTEM AND SURROUNDINGS

- A system is that part of universe which is under thermodynamic study and the rest of universe is called surroundings.
- A system is made up of one or more than one phase and is called homogenous and heterogenous systems respectively.

A phase is defined as homogenous, physically distinct and mechanically seperable portion of system.

Types of system:

Depending upon nature of boundary between system and surroundings:

(a) Isolated system: If the boundary prevents any interaction with the surroundings, the system is called isolated system.

Or

A system is said to be isolated when it can neither exchange energy nor matter with its surroundings.

e.g. – Boiling water, A cup of tea in thermus flask.

(b) Open system: If the matter & energy both can pass across the boundary, the system is called open system.

e.g. – Tea kept in cup.

(c) Closed system: If matter can't exchange but energy exchange it is called closed system.

e.g. – Tea kept in kettle.

Thermodynamic process:

It is the path or operation by which a system changes from one state to another.

1. **Isothermal process:** Temperature of system remains constant during each step.

$T = \text{constant.} \qquad dT = 0$

Details:

(i) For such change system should be contained in a perfectly coducting container.

(ii) Perfect isothermal change is impossible but when a change is carried out very slowly approximate isothermal change occurs.

(iii) It follows Boyle's law.

(iv) Work done in isothermal process is graphically given by area under P—V curve.

(v) $\Delta H = nC_P.\Delta T$ & $\Delta E = nC_V.\Delta T$

In isothermal process $\Delta T = 0$

$\therefore \quad \Delta H = 0 \quad \& \quad \Delta E = 0$

(vi) Specific heat at constant T is infinitely great in isothermal process.

2. **Adiabatic process:** There is no heat exchange between system & surroundings.

$q = \text{constant.} \qquad dq = 0$

Perfectly adiabatic change is impossible but when a process is carried out very rapidly fairly approximate adiabatic change occurs.

3. **Isobaric process:** It is the process in which pressure of the system remains constant during each step.

$P = \text{constant}$

$dP = 0$

4. **Polytropic process:** In this process heat capacity of the body remains constant.

$C_P = \text{constant}, \; C_V = \text{constant}$

$dC_P = 0 \;\&\; dC_V = 0$

5. **Quasistatic process:** The processs in which the deviation from thermodynamic equilibrium is infinitesimal & all the states through which the system passes can be considered as equilibrium states.

6. **Isochoric process:** When there is no change in the volume of the system du~~ring various operations~~ the change is said to be isochoric.

$V = \text{constant.} \qquad dV = 0$

The combustion of a substance in a bomb calorimeter is isochoric process.

7. **Cyclic process:** The process which brings back a system to its original state after a series of changes is called a cyclic process.

As the E & H depends only on their state.

$\therefore$ E & H = constant

& $dE = 0, \quad dH = 0$

Reversible process: A thermodynamically reversible process is one in which all changes occuring in any part of the process are exactly reversed when it is carried out in opposite direction.

Characteristics of reversible process:

1. It has to be carried out in infinitesimal amounts & hence require infinite time. Therefore changes in this process are very slow.
2. At all time, during the process, the driving force for the change is opposed by a restraining force infinitesimally smaller than the driving force.
3. It can be reversed by infinitesimal increase in opposing force.
4. The work produced in a reversible process is maximum.
5. A strictly reversible process is purely a concept.

e.g.– working of Daniell cell.

$Zn|ZnSO_4||CuSO_4|Cu$

This cell has a definite potential E. The cell is connected with a opposing source of potential i.e. Battery (E_{ext}).

Now, if

(a) $E = E_{ext}$, then no flows of current (no reversible change)

(b) $E > E_{ext}$, then current flows from cell & reaction is

$$Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$$

(c) $E < E_{ext}$, then direction of flow of current is reversed & chemical reaction is also reversed.

$$Zn^{2+} + Cu \longrightarrow Zn + Cu^{2+}$$

A slow process, in absence of frictional force, must be reversible when temperauture and pressure of the system and surroundings remains constant.

Irreversible process: The process which occurs suddenly or spontaneously without the restriction of occuring in successive stages of infinitesimal quantities.

For such process driving force is very much greater than opposing force; so these can't be reversed. These are also called spontaneous process.

Characteristics of irreversible process:

1. If the changes be reversed, the work in the forward direction & in the backward process would be unequal.
2. If initial & final stages be specified, the internal energy change would always be same, whether the process has been affected reversibly or irreversibly.
3. In an irreversible process, since work terms (dw) in two opposite directions are unequal, the heat transfers (dq) would also be unequal.
4. All natural processes are irreversible.

e.g. ⇒ (i) flow of heat from high temperature to low temperature;

(ii) Exapansion of gas from higher pressure to lower pressure.

Internal Energy:

Inernal energy is the energy associated with a system by virtue of its molecular consitution & motion of its molecules.

It depends upon internal potential energy & internal kinetic energy.

E_{Total} = Internal potential + Internal kinetic enegy

$$\boxed{E_{Total} = E_t + E_r + E_v + E_b + E_e + E_O + V_T + E_{nuc}}$$

where E_t = Translational K.E.

E_r = Rotational K.E.

E_V = Vibrational K.E.

E_b = Bond energy
E_e = Electronic energy
E_0 = Zero point energy
E_{nuc} = Energy due to interaction between nuclei.
V_T = Intermolecular interaction energy.

⇒ It is an extensive property (E & ΔE both).

⇒ Internal energy is a state function.

$$dE = E_2 - E_1 = E_{final} - E_{initial}$$

It follows Euler's theorem of Exactness.

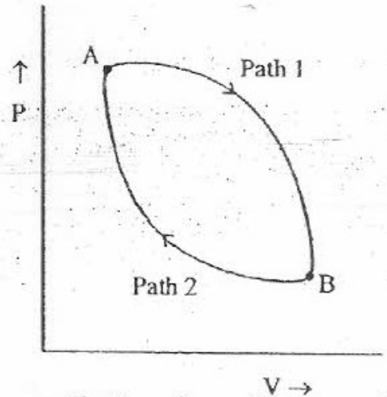
Sign of ΔE:

1. If $E_1 > E_2$, $\Delta E = -ve$

i.e. energy will be absorbed by the sytem from its surroundings. Hence reaction will be ~~exo~~endothermic.

⇒ For cyclic process

$$\sum \Delta E = 0 ; \oint dE = 0$$



Work: Any quantity that flows across the boundary of a system during a change in its state & is completely convertible into the lifting of a weight in the surroundings.

1. **Pressure - Volume work/work of expansion of gas:**

$$W = -(F_{ext} \times \text{distance through which piston moves } (\Delta\ell)) = -[F_{ext} \times \text{Area} \times (\Delta\ell)]$$

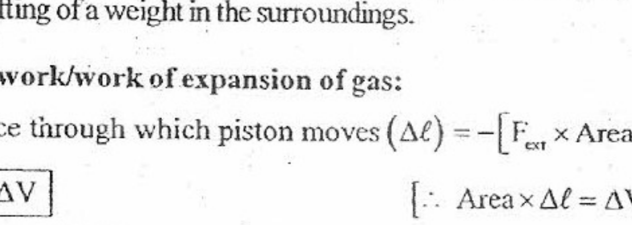
$$\boxed{W = -P_{ext}.\Delta V} \qquad [\because \text{Area} \times \Delta\ell = \Delta V]$$

Or $\boxed{W = -P_{ext}(V_2 - V_1)}$

(a) for expansion $V_2 > V_1$, thus W = negative

(b) for compression $V_1 > V_2$, thus W = positive

2. **Isothermal reversible expansion work of ideal gas**



Expansion will take place only when

$P_{int} > P_{ext}$

Where, P_{int} = Pressure exrted by gas (Internal Pressure)

P_{ext} = External pressure or atmospheric pressure

Work done, $W = -\int dW = -\int_{V_1}^{V_2} PdV;\ W = -\int_{V_1}^{V_2} pdV$ ...(1)

For an ideal gas, we know that $PV = nRT;\ P = \frac{nRT}{V}$

Putting this value of P in Equation (1), we get

$$W = \int_{V_1}^{V_2} \frac{nRT}{V} dV;\ W = -nRT \int_{V_1}^{V_2} \frac{dV}{V};\ W = -nRT\,[\ln V]_{V_1}^{V_2} = -nRT \ln\left(\frac{V_2}{V_1}\right)$$

$$\Rightarrow \quad W = -2.303\ nRT \log_{10}\left(\frac{V_2}{V_1}\right);\ \boxed{W = -2.303 nRT \log_{10}\left(\frac{V_2}{V_1}\right)}$$

Since $V_2 > V_1$ (due to expansion)

$$\Rightarrow \quad \frac{V_2}{V_1} > 1;\ \log_{10}\left(\frac{V_2}{V_1}\right) > 1;\ W < 0$$

i.e $W_{isothermal} < 0$

i.e. Work is done by the system.

Problem: If 2 mol of an ideal gas get expanded reversibly from $8 dm^3$ to $24 dm^3$. Then Calculate the total amount of heat in the isothermal process at 27°C.

Soln. We know that in case of reversible isothermal expansion of an ideal gas, the work done is given by-

$$W = -2.303\ nRT \log_{10}\left(\frac{V_2}{V_1}\right) \quad ...(1)$$

Here $n = 2$ (Two)

$T = 27°C = 27 + 273 = 300\ K$

R = gas constant $= 8.314 \frac{J}{K.mol}$

$V_1 = 8\ dm^3;\quad V_2 = 24\ dm^3$

Putting all these values in equation (1), we get

$$W = -2.303 \times (2\ mol) \times \left(8.314 \frac{J}{K\ mol}\right) \times \log_{10} \frac{24 dm^3}{8 dm^3} \times 300\ K$$

$\Rightarrow \quad W = -2.303 \times 2 \times 8.314 \times 300 \log_{10}(3)\ J$

$\Rightarrow \quad W = -2.303 \times 8.314 \times 600 \times 0.4771\ J$

$\Rightarrow \quad W = -5481.0608\ J$

Now from the first law of thermodynamics we know that $dQ = dU + dW$

$\Rightarrow \quad dQ = nC_V\, dT + dW$

$\Rightarrow \quad dQ = 0 + dW$

$[\because T = \text{constant}]\ (\because dT = 0)$

$\Rightarrow \quad Q = W$

$\therefore$ Total amount of heat $= +5481.0608\ J$

$$W_{rev} = -nRT\ell n \frac{V_2}{V_1} = -nRT\ell n \frac{P_1}{P_2}$$

3. Isothermal irreversible expansion work of an ideal gas

(i) Free expansion (in vacuum):

When an ideal gas is expanded isothermally in vacuum from a volume V_1 to V_2 irreversibly, Then

Work done $= -P_{ext}(V_2 - V_1)$ [$\therefore$ $w = -PdV$]

$= 0$ [Since in vacuum there is no external pressure on the gas]

(ii) When the ideal gas is expanded isothermally from a volume V_1 to V_2 irreversible upto a constant external pressure P_{ext} and if $P_{ext} < P_{gas}$, then

$$\boxed{\text{Work done} = -P_{ext}(V_2 - V_1)}$$

- * Is an adiabatic process
- * Sudden change in temperature takes place.
- * Cooling occurs very rapidly.

$= -R(T_2 - T_1)$

4. Reversible adiabatic expansion of an ideal gas:

Starting with the proof of $TV^{\gamma-1} = \text{constant}$

Proof: From the 1st law of thermodynamics, we know that,

$dQ = dU + dW$ (1)

But for an adiabatic process, Q is constant i.e $dQ = 0$

(1) $0 = dU + dW$; $dU + dW = 0$; $dU + dW = 0$

$\Rightarrow$ $nC_V\,dT + PdV = 0$ (2) [$dU = nC_V dT$ & $dW = PdV$]

For one mol $n = 1$

$\therefore$ (2) $\Rightarrow$ $C_V\,dT + PdV = 0$

$\Rightarrow$ $C_V\,dT + PdV = 0$ ... (3)

Now for one mole of an ideal gas, we know that

$$PV = RT; \; P = \frac{RT}{V}$$

Now putting this value of P in Euqation (3), we get

$$C_V\,dT + \left(\frac{RT}{V}\right)dV = 0; \; C_V\frac{dT}{T} + R\frac{dV}{V} = 0$$

$$\Rightarrow \quad C_V\frac{dT}{T} + (C_P - C_V)\frac{dV}{V} = 0 \qquad [\therefore R = C_P - C_V]$$

$$\Rightarrow \quad \frac{dT}{T} + \left(\frac{C_P}{C_V} - 1\right)\frac{dV}{V} = 0; \; \frac{dT}{T} + (\gamma - 1)\frac{dV}{V} = 0$$

Integrating both sides, we get $\int\frac{dT}{T} + (\gamma - 1)\int\frac{dV}{V} = 0$

$$\Rightarrow \quad \ln T + (\gamma - 1)\ln V = \ln C; \; \ln T + \ln V^{(\gamma-1)} = \ln C$$

$$\Rightarrow \quad \ln TV^{(\gamma-1)} = \ln C$$

Taking antilog, we get $TV^{(\gamma-1)} = C$

i.e. $\boxed{TV^{(\gamma-1)} = \text{constant}}$ ... (4)

Now, for 1 mol of an ideal gas, we know that,

$$PV = RT; \; T = \frac{PV}{R}$$

Putting this value of T in (4), we get

$$\left(\frac{PV}{R}\right)V^{(\gamma-1)} = \text{constant}$$

$\Rightarrow$ $\boxed{PV^{\gamma} = \text{constant}}$ ... (5)

[$\therefore$ R is also a constant]

Again, for one mol of an ideal gas, we have

$$PV = RT; \qquad V = \frac{RT}{P}$$

Now putting this value of V in equation (4). we get

$$T\left(\frac{RT}{P}\right)^{\gamma-1} = \text{constant}$$

$$\boxed{T^{\gamma}P^{(1-\gamma)} = \text{constant}}$$

Problem: A given mass of a gas at 0°C is compressed reversiblly and adiabatically to a pressure 20 times the initial value calculate the final temp of the gas.

($\gamma = 1.42$)

Soln. We know that,

$$T^{\gamma} P^{(1-\gamma)} = \text{Constant}$$

$\Rightarrow$ $T_1^{\gamma} P_1^{(1-\gamma)} = T_2^{\gamma} P_2^{(1-\gamma)}$; $\left(\frac{T_1}{T_2}\right)^{\gamma} = \left(\frac{P_2}{P_1}\right)^{(1-\gamma)}$ ... ①

Here,

$T_1 = 0°C = 273\text{ K}$, $T_2 = ?$, $P_1 = P_1$, $P_2 = 20P_1$ & $\gamma = 1.42$

Putting all there values in Equation (1), we get

$$\left(\frac{273}{T_2}\right)^{1.42} = \left(\frac{20P_1}{P_1}\right)^{1-1.42}; \left(\frac{273}{T_2}\right)^{1.42} = (20)^{-0.42}$$

Taking log, we get, $1.42 \log_{10}\left(\frac{273}{T_2}\right) = -0.42 \log_{10}(20)$

$\Rightarrow$ $1.42 \log_{10}(273) - 1.42 \log_{10} T_2 = -0.42 \log_{10}(2\times10)$

$\Rightarrow$ $1.42 \log_{10} T_2 = 1.42 \log_{10} 273 + 0.42 \left[\log_{10} 2 + \log_{10} 10\right]$

$\log_{10} T_2 = 4.00577/1.42 = 2.820965$

$\Rightarrow$ Taking anti log $= 10^{2.820965} = 66.2.16\text{ K}$

5. **Work done in reversible adiabatic expansion for an ideal gas:**

$\int dw = -\int_{V_1}^{V_2} PdV$ ... (i)

$\Rightarrow$ $w = -\int_{V_1}^{V_2} PdV$ (ii)

Now we know that for adiabatic process, $PV^{\gamma} = \text{constant}$

$\Rightarrow$ $PV^{\gamma} = K$; $P = KV^{\gamma-}$

Also $P_1V_1^{\gamma} = P_2V_2^{\gamma} = K$ ... (iii)

Now putting this value of P in equation (ii), we get

$$w = -\int_{V_1}^{V_2} KV^{-\gamma}dV;\ w = -K\int_{V_1}^{V_2} V^{-\gamma}dV;\ w = -K\left[\frac{V^{-\gamma+1}}{-\gamma+1}\right]_{V_1}^{V_2};\ w = \frac{-K}{1-\gamma}\left[V_2^{1-\gamma} - V_1^{1-\gamma}\right]$$

$\Rightarrow \quad w = \frac{-1}{(1-\gamma)}\left[KV_2^{1-\gamma} - KV_1^{1-\gamma}\right];\ w = \frac{1}{(\gamma-1)}\left[P_2V_2^{\gamma}V_2^{1-\gamma} - P_1V_1^{\gamma}V_1^{1-\gamma}\right]$ [Using (iii)]

$\Rightarrow \quad \boxed{w = \frac{1}{(\gamma-1)}(P_2V_2 - P_1V_1)}$ ... (iv)

Now for an ideal gas, we know that, $PV = nRT$

$\Rightarrow \quad P_1V_1 = nRT_1$ ... (v)

& $\quad P_2V_2 = nRT_2$ ... (vi)

(vi)–(v) $\Rightarrow \quad P_2V_2 - P_1V_2 = nR(T_2 - T_1)$

Now making this substitution in equation (iv), we get

$\boxed{w = \frac{1}{(\gamma-1)}nR(T_2 - T_1)}$

6. Work done in irreversible adiabatic expansion for an ideal gas:

(i) Free expansion (in Vacuum):

When an ideal gas is expanded adiabatically (in vacuum) from a volume V_1 to V_2 irreversibly, Then

work done $= -P_{ext}(V_2 - V_1)$

$= 0$

[Since in vacuum there is no external pressure on the gas]

(ii) When the ideal gas is expanded adiabatically from a volume V_1 to V_2 irreversibly upto a constant external pressure P_{ext} and if $P_{ext} < P_{gas}$, Then

Work done $= -P_{ext}(V_2 - V_1)$ ... (i)

Now from the 1st low of thermodynamics, we know that

$dQ = dU + dW$

$0 = dU + dW$ [$\therefore$ For adiabatic Process Q = constt]

$\Rightarrow \quad 0 = nC_VdT + PdV;\ 0 = nC_V(T_2 - T_1) + P(V_2 - V_1)$

$\Rightarrow \quad -P(V_2 - V_1) = nC_V(T_2 - T_1);\ (V_2 - V_1) = -\frac{nC_V}{P}(T_2 - T_1)$

Now making this substitution in equation (i), we get

$\Rightarrow \quad$ Work done $= nC_V\frac{P_{ext}}{P}(T_2 - T_1)$ [Where, P is pressure of the gas]

Problem: Two moles of a monoatomic gas expand adiabatically in a reversible manner on heating 27°C to 327°C. Then calculate total change in internal energy of the entire process.

Soln: We know that, chnage in internal energy (dU) is given as

$dU = nC_VdT$

$\Rightarrow \quad dU = nC_V(T_2 - T_1)$ ... (i)

Here, dU = change in internal energy.

n = 2 moles

$C_V = \frac{3}{2}R \left[\because \text{For monoatomic gas } C_V = \frac{3}{2}R\right]$

$T_1 = 27°C = (27 + 273)\ K = 300\ K$

$T_2 = 327°C = (327 + 273)\ K = 600\ K$

Now putting all these values in Equation (i), we get change in internal energy

$\Rightarrow \quad dU = 2mol \times \frac{3}{2} \times R(600 - 300)\ K = 3 \times 2 \times \frac{cal}{k.mol} \times 300\ mol\ K$

$\Rightarrow \quad dU = 1800\ cal$

Second Method:

We know that, work done in reversible adiabatic expansion (w) is given as:

$$w = \frac{1 \times nR}{(\gamma - 1)}(T_2 - T_1) = \frac{nR}{\left(\frac{C_P}{C_V} - 1\right)}(T_2 - T_1) = \frac{n(C_P - C_V)}{\left(\frac{C_P - C_V}{C_V}\right)}(T_2 - T_1) = \frac{nC_V R}{R}(T_2 - T_1) = nC_V dT$$

$= dU$ (Change in internal energy)

i.e. in reversible adiabatic expansion, the work done is equal to the change in internal energy.

Zeroth Law of Thermodynamics:

If body A is in equilibrium with body C & body B is also in equilibrium with body C, then bodies A & B are in equilibrium with each other

First law of thermodynamics:

It is the law of conversation of energy & can be stated in various ways.

1. "The total mass & energy of an isolated system remains constant"
2. "Energy can be transformed from one form to another form but energy can neither be created nor destroyed."
3. It is impossible to construct a perpetual motion machines which could produce work without consuming any energy."

Mathematically, $\boxed{dU = dq + dw}$

$$\text{State A} \longrightarrow \text{State B};\ \int_A^B dU = \int_A^B dq + \int_A^B dw;\ U_B - U_A = q + w$$

Or $\boxed{\Delta U = q + w}$ ... (1)

It may be noted that the values of both q & w depend upon the path followed in going from state A to state B, but the algebraic sum of these two quantities is independent of the path. Thus (q+w) is state function.

At constant volume $dV = 0$

$W = -P_{ex}\,dV = 0$

∴ from equation (1)

$\boxed{\Delta U = q_v}$

Thus heat absorbed at constant volume increases the internal energy.

At constant temperature $\Delta U = 0$

∴ $q + w = 0;\ q = -w$

Thus amount of heat absorbed by the system from the surroundings is equal to the work done by the system on the surroundings.

⇒ **For cyclic process** $\Delta U = 0$

∴ $q + w = 0$

⇒ **At constant pressure**

$q_p = H =$ enthalpy

∴ first law becomes

$\Delta U = H + W$

⇒ **For adiabatic process** $q = 0$

∴ $\Delta U = 0 + W;\ \Delta U = W;\ \Delta U = -P_{ext}(\Delta V)$

Thus work is equal to the loss in internal energy.

Enthalpy/heat content (H):

Thermal changes occuring at constant pressure is called as enthalpy.

$H = U + PV$ ... (1)

Or $dH = dU + PdV + VdP$ ... (2)

⇒ H is a state function & dH is an exact differential.

from equation (1)

$$H_1 = U_1 + P_1V_1 \qquad \& \qquad H_2 = U_2 + P_2V_2$$

$$\therefore \quad \Delta H = H_2 - H_1 = (U_2 + P_2V_2) - (U_1 + P_1V_1) = (U_2 - U_1) - (P_2V_2 - P_1V_1)$$

$$\Delta H = \Delta U + P(V_2 - V_1) \qquad \text{[At constant pressure } P_2 = P_1 = P\text{]}$$

$$\boxed{\Delta H = \Delta U + P\Delta V} \quad \text{... (3)}$$

Or $$\boxed{\Delta H = \Delta U + W} \quad \text{... (4)}$$

From Ist law

$\Delta U = q - w$

∴ equation (4) becomes.

$$\Delta H = q - w + w \, ; \boxed{\Delta H = q_p}$$

⇒ $\boxed{\begin{array}{l}\text{If } \Delta H = +\text{ve, process will be endothermic} \\ \text{If } \Delta H = -\text{ve, process will exothermic.}\end{array}}$

Relation between ΔH & ΔU :

From first law, $\Delta U = q - w \, ; \, \Delta U = q - P\Delta V$

at constant volume $\Delta V = 0 \, ; \boxed{\Delta U = q_V}$

Again we know, $\Delta H = q_P$

Therefore, from equation (3)

$$\Delta H = \Delta U + P\Delta V$$

Let n_1 moles of gaseous reactant changes into n_2 mole of gaseous product under constant T & P.

$$\therefore \quad PV_1 = n_1RT \, ; \, PV_2 = n_2RT \qquad \therefore \qquad PV_2 - PV_1 = n_2RT - n_1RT$$

$P\Delta V = \Delta n_g RT$ $\qquad \Delta n_g$ = (mole of gaseous product) – (moles of gaseous reactant)

$$\therefore \quad \boxed{\Delta H = \Delta E + \Delta n_g RT} \quad \text{... (5)}$$

Application of First Law of Thermodynamics:

1. **Heat capacity:** The heat required to raise the temperature by one degree.

It is of two types:

(a) Specific heat capacity: It is the amount of heat absorbed by 1 gm of a substance to raise its temperature by 1°C.

$$\boxed{C = \frac{q}{m(T_2 - T_1)}}$$

(b) Molar heat capacity: It is the amount of heat absorbed by 1 mole of a substance to raise its temperature by 1°C.

$$C = \frac{q}{n(T_2 - T_1)} \, ; \, C \times n = \frac{q}{(T_2 - T_1)} \, ; \, C_M = \frac{q}{(T_2 - T_1)} \, ; \boxed{C = \frac{dq}{dT}}$$

From first law $dq = dU + Pdv$

$$\therefore \quad \boxed{C = \frac{dU + PdV}{dT}}$$

(i) At constant volume: $dV=0$

$$C_V=\left(\frac{dU}{dT}\right)_V;\ \boxed{C_V=\left(\frac{\partial U}{\partial T}\right)_V}$$

(ii) At constant pressure: $(dq)_P=(dH)_P$

$$dH=dU+PdV$$

$$\therefore\ \boxed{C_P=\left(\frac{dH}{dT}\right)_P}$$

Various (C_P-C_V) relations:

Problem: Show that

(i) $C_P-C_V=T\left(\frac{\partial P}{\partial T}\right)_V\cdot\left(\frac{\partial V}{\partial T}\right)_P$ (ii) $C_P-C_V=R$ for ideal gas.

(iii) $C_P-C_V=R\left(1+\frac{2a}{RTV}\right)$ for real gas (iv) $C_P-C_V=\frac{\alpha^2TV}{\beta}$

(v) $C_P-C_V=-T\left(\frac{\partial P}{\partial T}\right)_V^2\left(\frac{\partial V}{\partial P}\right)_T$

Soln. (i) $\boxed{C_P-C_V=T\left(\frac{\partial P}{\partial T}\right)_V\cdot\left(\frac{\partial V}{\partial T}\right)_P}$

Let $S=f(V,T)$

On complete differential

$$dS=\left(\frac{\partial S}{\partial V}\right)_T.dV+\left(\frac{\partial S}{\partial T}\right)_V.dT$$

$$TdS=T\left(\frac{\partial S}{\partial V}\right)_T.dV+T\left(\frac{\partial S}{\partial T}\right)_V.dT \qquad \left[\left(T\left(\frac{\partial S}{\partial T}\right)_V\right)=C_V\right]$$

$ds=\frac{dq}{T}$

$\Rightarrow dq=T\,dS$

$c_v=\frac{dq}{dT}=T\frac{dS}{dT}$

$$TdS=T\left(\frac{\partial S}{\partial V}\right)_T.dV+C_V.dT$$

Divide by dT ~~at constant pressure~~

$$\left(\frac{TdS}{dT}\right)_P=T\left(\frac{\partial S}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P+C_V\left(\frac{dT}{dT}\right)_P$$

$$C_P=T\left(\frac{\partial S}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P+C_V$$

$$C_P-C_V=T\left(\frac{\partial S}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P$$

From thermodynamic square

$$\left(\frac{\partial S}{\partial V}\right)_T=\left(\frac{\partial P}{\partial T}\right)_V$$

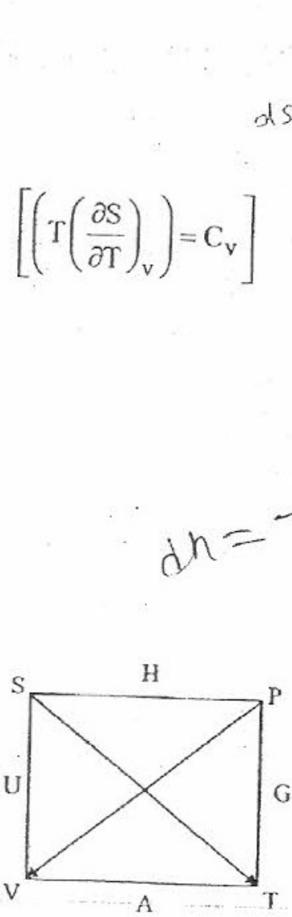
$dh=Tds+vdP$

$dG=-VdP+SdT$

$dA=-PdV-SdT$

$dU=TdS+PdV$

$(dU)_{S,V}\leq 0$



$$\therefore \quad \boxed{C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V . \left(\frac{\partial V}{\partial T}\right)_P}$$

⇒ The above relation is called as standard equation various relations can be derived by using this rule.

(ii) $\boxed{C_P - C_V = R}$ for ideal gas

$$\begin{bmatrix} \text{for ideal gas} \\ PV = RT \\ P = \dfrac{RT}{V} \\ \& \ V = \dfrac{RT}{P} \end{bmatrix}$$

From standard equation.

$$C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P$$

$$\therefore \quad C_P - C_V = T\left(\frac{\partial}{\partial T}\frac{RT}{V}\right)_V \left(\frac{\partial}{\partial T}\frac{RT}{P}\right)_P$$

$$C_P - C_V = \frac{TR}{V}\left(\frac{\partial T}{\partial T}\right)_V \times \frac{R}{P}\left(\frac{\partial T}{\partial T}\right)_P = \frac{TR}{V}.\frac{R}{P} = P \times \frac{R}{P}$$

$$\boxed{C_P - C_V = R}$$

Proved.

(iii) $C_P - C_V = R\left(1 + \frac{2a}{RTV}\right)$ for real gas:

From standard equaion,

$$C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V . \left(\frac{\partial V}{\partial T}\right)_P \quad \dots(1)$$

Now we put value of P & V from vander waal's equation

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \quad \dots(2)$$

$$\left(P + \frac{a}{V^2}\right) = \frac{RT}{(V-b)}; \ P = \left[\frac{RT}{(v-b)} - \frac{a}{v^2}\right]$$

$$\therefore \quad \left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial}{\partial T}\frac{RT}{(V-b)}\right)_V - \underset{\substack{\Downarrow \\ 0}}{\left(\frac{\partial}{\partial T}\frac{a}{V^2}\right)_V}; \ \left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{R}{V-b}\right) \quad \dots(3)$$

Again differentiation equation (2) w.r.t temperature at constant pressure

$$\overset{\text{I}}{\left[\frac{\partial}{\partial T}\left(P + \frac{a}{V^2}\right)(V-b)\right]_P} = \overset{\text{II}}{\left(\frac{\partial}{\partial T}RT\right)_P}$$

$$\left(P + \frac{a}{V^2}\right)\left[\frac{\partial}{\partial T}(V-b)\right]_P + (V-b)\left\{\frac{\partial}{\partial T}\left(P + \frac{a}{V^2}\right)\right\}_P = R\left(\frac{\partial T}{\partial T}\right)_P + T\underset{\substack{\Downarrow \\ 0}}{\left(\frac{\partial R}{\partial T}\right)_P}$$

$$\left(P + \frac{a}{V^2}\right)\left(\frac{\partial V}{\partial T}\right)_P - \underset{\substack{\Downarrow \\ 0}}{\left(\frac{\partial b}{\partial T}\right)_P} + (V-b)\left[\underset{\substack{\Downarrow \\ 0}}{\left(\frac{\partial P}{\partial T}\right)_P} + \left(\frac{\partial}{\partial T}\frac{a}{V^2}\right)_P\right] = R$$

$$\therefore \left(P+\frac{a}{V^2}\right)\left(\frac{\partial V}{\partial T}\right)_P+(V-b)\left[\frac{-2a}{V^3}\left(\frac{\partial V}{\partial T}\right)_P\right]=R\ ;\ \frac{RT}{(V-b)}\left(\frac{\partial V}{\partial T}\right)_P-\frac{2a}{V^3}(V-b)\left(\frac{\partial V}{\partial T}\right)_P=R$$

$$\left(\frac{\partial V}{\partial T}\right)_P=\frac{R}{\left[\frac{RT}{(V-b)}-\frac{2a(V-b)}{V^3}\right]} \qquad \dots(4)$$

Putting value of equation (3) & (4) in equation (1)

$$C_P-C_V=T\times\frac{R}{(V-b)}\times\frac{R}{\left[\frac{RT}{(V-b)}-\frac{2a(V-b)}{V^3}\right]}$$

$$C_P-C_V=\frac{RT}{(V-b)}\times\frac{R}{\frac{RT}{(V-b)}\left[1-\frac{2a(V-b)^2}{V^3RT}\right]} \qquad \text{So,} \quad V>b,(V-b)^2\approx V^2$$

$$=\frac{R}{1-\frac{2aV^2}{V^3RT}}=R\left[1-\frac{2a}{RTV}\right]^{-1} \quad \text{Let } (V-b=V)$$

$$\boxed{C_P-C_V=R\left[1+\frac{2a}{RTV}\right]}$$

Proved.

(iv) $C_P-C_V=\frac{\alpha^2TV}{\beta}$ for ideal gas:

$$\because \quad \alpha=\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P, \qquad \beta=-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

$$\therefore \quad C_P-C_V=\frac{\left[\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P\right]^2\times T\times V}{-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T}=\frac{\frac{1}{V^2}\left(\frac{\partial V}{\partial T}\right)_P^2\times T\times V}{-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T}$$

$$C_P-C_V=-T\left(\frac{\partial V}{\partial T}\right)_P\cdot\underbrace{\left(\frac{\partial V}{\partial T}\right)_P\cdot\left(\frac{\partial P}{\partial V}\right)_T}$$

From cyclic rule.

$$\left(\frac{\partial V}{\partial T}\right)_P\left(\frac{\partial T}{\partial P}\right)_V\left(\frac{\partial p}{\partial V}\right)_T=-1;\quad \left(\frac{\partial V}{\partial T}\right)_P\left(\frac{\partial P}{\partial V}\right)_T=-\frac{1}{\left(\frac{\partial T}{\partial P}\right)_V}$$

$$\therefore \quad C_P-C_V=-T\left(\frac{\partial V}{\partial T}\right)_P\times-\left(\frac{\partial P}{\partial T}\right)_V=T\left(\frac{\partial V}{\partial T}\right)_P\left(\frac{\partial P}{\partial T}\right)_V$$

Thus standard rule proves validity of given relation.

(v) $C_P - C_V = -T\left(\frac{\partial P}{\partial T}\right)^2\left(\frac{\partial V}{\partial P}\right)_T$

From fundamental rule.

$$C_P - C_V = T\left(\frac{\partial V}{\partial T}\right)_P \cdot \left(\frac{\partial P}{\partial T}\right)_V$$

From cyclic rule.

$$\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \cdot \left(\frac{\partial T}{\partial P}\right)_V = -1; \quad \left(\frac{\partial V}{\partial T}\right)_P = \frac{-1}{\left(\frac{\partial P}{\partial V}\right)_T \cdot \left(\frac{\partial T}{\partial P}\right)_V}$$

$$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial V}{\partial P}\right)_T \cdot \left(\frac{\partial P}{\partial T}\right)_V \qquad \left[\begin{array}{l}\text{using Euler's theorem}\\ \dfrac{1}{\left(\frac{\partial P}{\partial V}\right)_T} = \left(\frac{\partial V}{\partial P}\right)_T\end{array}\right]$$

$$\therefore \quad C_P - C_V = T\left[-\left(\frac{\partial V}{\partial P}\right)_T \cdot \left(\frac{\partial P}{\partial T}\right)_V\right]\left(\frac{\partial P}{\partial T}\right)_V$$

$$\boxed{C_P - C_V = -T\left(\frac{\partial V}{\partial P}\right)_T \cdot \left(\frac{\partial P}{\partial T}\right)_V^2}$$

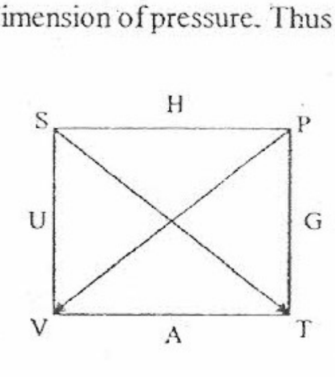
Proved.

FIRST THERMODYNAMIC EQUATION OF STATE

Change in internal energy with respect to volume at constant temp. is known as first thermodynamic equation of state.

Dimensionally it was seen that its dimension is the dimension of pressure. Thus it is also called as internal pressure (π)

From thermodynamic square



$$dU = TdS - PdV$$

$$\therefore \quad \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P\left(\frac{\partial V}{\partial V}\right)_T$$

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P$$

from thermodynamic square

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V; \quad \boxed{\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P}$$

Or $$\boxed{\pi = T\left(\frac{\partial P}{\partial T}\right)_V - P} \qquad \ldots(1)$$

For ideal gas $\pi = 0$:

From equation (1)

$$\pi = T\left(\frac{\partial}{\partial T}\frac{RT}{V}\right)_V - P = T\frac{R}{V}\left(\frac{\partial T}{\partial T}\right)_V - P = \frac{RT}{V} - P = P - P = 0 \qquad \pi = 0 \text{ for ideal gas}$$

For real gas $\pi = \frac{a}{v^2}$:

For real gas; $\left(P+\frac{a}{v^2}\right)(v-b) = RT$; $P = \left[\left(\frac{RT}{v-b}\right) - \frac{a}{V^2}\right]$

$$\therefore \quad \pi = T\left(\frac{\partial}{\partial T}\frac{RT}{(v-b)}\right)_v - \underset{\overset{\Downarrow}{0}}{\left(\frac{\partial}{\partial T}\frac{a}{V^2}\right)_v} - P = T\frac{R}{(v-b)}\left(\frac{\partial T}{\partial T}\right)_v - P \qquad \boxed{\pi = \frac{a}{V^2}}$$

$$= \frac{RT}{(v-b)} - P = \left(P+\frac{a}{V^2}\right) - P \qquad \left[\because \left(P+\frac{a}{v^2}\right) = \frac{RT}{(v-b)}\right]$$

$$\boxed{\pi_T = \frac{a}{V^2}}, \quad \boxed{\text{for n moles} = \frac{n^2a}{V^2}}$$

SECOND THERMODYNAMIC EQUATION OF STATE

Change in enthalpy w.r.t pressure at consant temperature is known as second thermodynamic equation of state.

$$dH = TdS + VdP$$

$$\left(\frac{\partial H}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T + V\left(\frac{\partial P}{\partial P}\right)_T; \quad \left(\frac{\partial H}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T + V$$

From thermodynamic square, $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$

$$\boxed{\therefore \quad \left(\frac{\partial H}{\partial P}\right)_T = \left[-T\left(\frac{\partial V}{\partial T}\right)_P + V\right]} \qquad \ldots(1)$$

For ideal gas $\left(\frac{\partial H}{\partial P}\right)_T = 0$

$$\left(\frac{\partial H}{\partial P}\right)_T = -T\left(\frac{\partial}{\partial T}\frac{RT}{P}\right)_P + V = -T\frac{R}{P}\left(\frac{\partial T}{\partial T}\right)_P + V = -V + V; \ \left(\frac{\partial H}{\partial P}\right)_T = 0$$

Problem: Show that for fixed amount of ideal gas $\left(\frac{\partial C_V}{\partial V}\right)_T = 0$

Soln. $\left(\frac{\partial C_V}{\partial V}\right)_T = \left[\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial T}\right)_V\right]_T$ From Euler's theorem.

$\left[\frac{\partial}{\partial T}\left(\frac{\partial U}{\partial V}\right)_T\right]_V$ But $\left(\frac{\partial U}{\partial V}\right)_T = 0$ for ideal gas

$\therefore \quad \left(\frac{\partial C_V}{\partial V}\right)_T = 0$ **proved.**

2. **Variation of heat of reaction temperature**

(For low range of temp)

Two Relation

ΔC_P $\quad \Delta H_2$ $\quad \Delta H_1$

$\quad T_2$ $\quad T_1$

ΔC_V $\quad \Delta E_2$ $\quad \Delta E_1$

$\quad T_2$ $\quad T_1$

Consider the equation, $aA + bB \rightarrow cC + dD$

(Where, a, b, c, & d are stoichiometric Coefficicents)

$$\Delta H = \sum H_P - \sum H_R$$

$$\Rightarrow \quad \Delta H = (cH_C + dH_D)_{\text{product}} - (aH_A + bH_B)_{\text{reactant}}$$

$$\Rightarrow \quad \left[\frac{\partial(\Delta H)}{\partial T}\right]_P = \left[c\left(\frac{\partial H_C}{\partial T}\right)_P + d\left(\frac{\partial H_D}{\partial T}\right)_P\right]_{\text{Product}} - \left[a\left(\frac{\partial H_A}{\partial T}\right)_P + b\left(\frac{\partial H_B}{\partial T}\right)_P\right]_{\text{Reactant}}$$

$$\Rightarrow \quad \left(\frac{\partial(\Delta H)}{\partial T}\right)_P = \left[\underset{\text{Specific heat Capacities of Product}}{c\,C_P(C) + d\,C_P(D)}\right]_{\text{Product}} - \left[\underset{\text{Specific heat Capacities of Reactant}}{a\,C_P(A) + b\,C_P(B)}\right]_{\text{Reactant}}$$

$$\Rightarrow \quad \left[\frac{\partial(\Delta H)}{\partial T}\right]_P = (C_P)_{Product} - (C_P)_{Reactant}; \quad \left[\frac{\partial(\Delta H)}{\partial T}\right]_P = \Delta C_P; \quad d(\Delta H) = \Delta C_P\, dT$$

$$\Rightarrow \quad \int_{T_1}^{T_2} d(\Delta H) = \int_{T_1}^{T_2} \Delta C_P\, dT \qquad \ldots(i)$$

If at $T = T_1$, $\Delta H = \Delta H_1$ & $T = T_2$, $\Delta H = \Delta H_2$

Then (i)

$$\Rightarrow \quad \Delta H_2 - \Delta H_1 = \Delta C_P (T_2 - T_1)$$

$$\Rightarrow \quad \boxed{\Delta H_2 = \Delta H_1 + \Delta C_P (T_2 - T_1)} \qquad \ldots(ii)$$

Similarly, $\boxed{\Delta E_2 = \Delta E_1 + \Delta C_V (T_2 - T_1)}$ ... (iii)

There Equation (ii) & (iii) are known as 'Kirchoff's Equations'.

If Temp. range is not low (i.e. high) then C_P, C_V vary with temp. as-

$\boxed{C_P = \alpha + \beta T + \gamma T^2}$; $\boxed{\Delta C_P = \Delta\alpha + \Delta\beta T + \Delta\gamma T^2}$

For the reaction

$aA + bB \rightarrow cC + dD$

$\Delta\alpha = (c\alpha_C + d\alpha_D) - (a\alpha_A + b\alpha_B)$; $\Delta\beta = (c\beta_C + d\beta_D) - (a\beta_A + b\beta_B)$

$\Delta\gamma = (c\gamma_C + d\gamma_D) - (a\gamma_A + b\gamma_B)$

In this case kirchoff's equation is derived as

$$(M) \quad \Rightarrow \quad \left[\frac{\partial(\Delta H)}{\partial T}\right]_P = \Delta C_P; \quad \left[\frac{\partial(\Delta H)}{\partial T}\right]_P = \Delta\alpha + \Delta\beta T + \Delta\gamma T^2$$

$$\Rightarrow \quad \int_{T_1}^{T_2} d(\Delta H) = \int_{T_1}^{T_2} [\Delta\alpha + \Delta\beta T + \Delta\gamma T^2]\, dT; \quad \Delta H_2 - \Delta H_1 = \int_{T_1}^{T_2} \Delta\alpha\, dT + \int_{T_1}^{T_2} \Delta\beta T\, dT + \int_{T_1}^{T_2} \Delta\gamma T^2\, dT$$

$$\Rightarrow \quad \boxed{\Delta H_2 - \Delta H_1 = \Delta\alpha(T_2 - T_1) + \frac{\Delta\beta}{2}(T_2^2 - T_1^2) + \frac{\Delta\gamma}{3}(T_2^3 - T_1^3)}$$

Problem: The enthalpy of reaction ΔH for the formation of ammonia according to the reaction

$N_2 + 3H_2 \rightleftharpoons 2NH_3$

at 27°C was found to be – 91.94 kJ.

What willbe the enthalpy of reaction ΔH at 50°C?

Molar heat capacities at constant pressure and at 27°C for N_2, H_2 & NH_3 are 28.45, 28.32 & 37.07 Joules/K respectively,

Soln: From Kirchoff's equtaion we have

$\Delta H_2 = \Delta H_1 + \Delta C_P (T_2 - T_1)$ ... (i)

Here $T_1 = 27°C = (27 + 273)\ K = 300K$ ... (ii)

$T_2 = 50°C = (50 + 273)\ K = 323\ K$ ... (iii)

$\Delta H_1 = -91.94\ KJ = -91.94 \times 10^3 J$ ... (iv)

$\Delta C_P = 2C_P(NH_3) - [C_P(N_2) + 3\ C_P(H_2)]$ ... (v)

$\Rightarrow \quad \Delta C_P = 2 \times 37.07\ J/K - [28.45 + 3 \times 28.32]\ J/K$ ... (v)

$\Rightarrow \quad \Delta C_P = -39.27\ /J/K \quad \& \ \Delta H_2 = ?$ ... (vi)

Now making substitution from the equation (ii), (iii) (iv) & (v) in equation (i), we get

$\Delta H_2 = -91.94 \times 10^3\ J + (-39.27)\ [323–300] = -91.94 \times 10^3\ J - 39.27 \times 23\ J$

$= -91.94 \times 10^3\ J - 903.21\ J = -92843.21\ J$

Problem: Calculate enthalpy change at 125°C for the reaction

$N_2 + 3H_2 \rightleftharpoons 2NH_3;\ \Delta H_{298} = -92.41$ kJ

The molar heat capacities in (J K^{-1} for the various gases involved in the reaction vary with temp as

$C_p(N_2) = 27.26 + 5.\ 23 - 10^{-3}\,T - 4.18 \times 10^{-9}T^2$

$C_p(H_2) = 29.02 - 8.35 \times 10^{-4}\,T + 20.\ 80 \times 10^{-7}\,T^2$

$C_p(NH_3) = 25.86 + 32.94 \times 10^{-2}\,T + 30.02 \times 10^{-7}\,T^2$

Soln: From Kirchoff's equation, we have

$$\Delta H_2 = \Delta H_1 + \Delta\alpha\,(T_2 - T_1) + \frac{\Delta\beta}{2}(T_2^2 - T_1^2) + \frac{\Delta\gamma}{3}(T_2^3 - T_1^3) \quad \text{... (i)}$$

Here $T_1 = 298$ K ... (ii)

$T_2 = 125\ °C = (125 + 273)K = 398$ K ... (iii)

$\Delta H_1 = -92.41$ kJ $= -92.41 \times 10^3$ J ... (iv)

$\Delta\alpha = 2\alpha(NH_3) - [\alpha(N_2) + 3\alpha(H_2)]$ ... (v)

$\Delta\beta = 2\beta(NH_3) - [\beta(N_2) + 3\beta(H_2)]$ ... (vi)

$\Delta\gamma = 2\gamma(NH_3) - [\gamma(N_2) + 3\gamma(H_2)]$ ... (vii)

Here, $\alpha(N_2) = 27.26,\ \beta(N_2) = 5.23 \times 10^{-3},\ \gamma(N_2) = -4.18 \times 10^{-9}$

$\alpha(H_2) = 29.02,\ \beta(H_2) = -8.35 \times 10^{-4},\ \gamma(H_2) = 20.80 \times 10^{-7}$

$\alpha(NH_3) = 25.86,\ \beta(NH_3) = 32.94 \times 10^{-2},\ \gamma(NH_3) = 30.02 \times 10^{-7}$

$\therefore\quad (V) \Rightarrow \Delta\alpha = 2 \times 25.86 - [27.26 + 3 \times 29.02]$

$\Rightarrow\quad \Delta\alpha = 51.72 - [27.26 + 87.06];\ \Delta\alpha = 51.72 - [114.32]$

$\Rightarrow\quad \Delta\alpha = -62.60$ ... (viii)

Now

$(VI) \Rightarrow \Delta\beta = 2 \times 32.94 \times 10^{-2} - [5.23 \times 10^{-3} + 3 \times (-8.35 \times 10^{-4})]$

$\Rightarrow\quad \Delta\beta = 65.88 \times 10^{-2} - [5.23 \times 10^{-3} - 25.05 \times 10^{-4}]$

$\Rightarrow\quad \Delta\beta = 65.88 \times 10^{-2} - [0.523 \times 10^{-2} - 0.2505 \times 10^{-2}]$

$\Rightarrow\quad \Delta\beta = 65.1065 \times 10^{-2}$ ... (ix)

Now (viii)

$\Delta\gamma = 60.04 \times 10^{-7} - [-4.18 \times 10^{-9} + 3 \times 20.80 \times 10^{-7}]$

$\Delta\gamma = 60.04 \times 10^{-7} - [-0.0418 \times 10^{-7} + 62.40 \times 10^{-7}]$

$\Rightarrow\quad \Delta\gamma = (60.04 + 0.0418 - 62.40) \times 10^{-7}$

$\Rightarrow\quad \Delta\gamma = (60.0818 - 62.40) \times 10^{-7}$

$\Rightarrow\quad \Delta\gamma = -2.3182 \times 10^{-7}$ ... (x)

Now making substitution from the equations (ii), (iii), (iv), (viii), (ix) & (x) equ. (i), we get

$$\Delta H_2 = -92.41 \times 10^3 + (-62.60)(398 - 298) + \left(\frac{65.1065 \times 10^{-2}}{2}\right)[398^2 - 298^2] + \left(\frac{-2.3182 \times 10^{-7}}{3}\right)[398^3 - 298^3]$$

$\Rightarrow\quad \Delta H_2 = -92.41 \times 10^3 - 62.60 \times 100 + 32.55325 \times 10^{-2} \times 69600 + [-0.7727333 \times 10^{-7}] \times 36581200$

$\Rightarrow\quad \Delta H_2 = -92.41 \times 10^3 - 6.260 \times 10^3 + 2265706.2 \times 10^{-2} + [-28267511 \times 10^{-7}]$

$\Rightarrow\quad \Delta H_2 = -98.670 \times 10^3 + 22.657062 \times 10^3 - 0.0028267511 \times 10^3$

$\Rightarrow\quad \Delta H_2 = -(-98.6728267511 + 22.657062) \times 10^3;\ \Delta H_2 = -76.02 \times 10^3$ J

$\Rightarrow\quad \Delta H_2 = -76.02$ kJ

Problem: Prove that for reversible process $\oint w = 0$

Soln. Let a gas is expanding from an initial volume of V_1 to a final volume V_2. Thus reversible work

$$w_1 = -2.303RT\log\frac{V_2}{V_1}$$

Now the gas is compressed from $V_2 \rightarrow V_1$

$$w_2 = -2.303RT\log\frac{V_1}{V_2} = 2.303RT\log\frac{V_2}{V_1}$$

∴ Total cyclic work.

$$\oint w = w_1 + w_2 = -2.303RT\log\frac{V_2}{V_1} + 2.303RT\log\frac{V_2}{V_1}$$

Problem: For irreversible process $\oint w \neq 0$

Let a gas expanding irreversibly from $V_1 \rightarrow V_2$ against external pressure P_2.

$$w_{exp} = -P_2\,ext\left(V_2 - V_1\right)$$

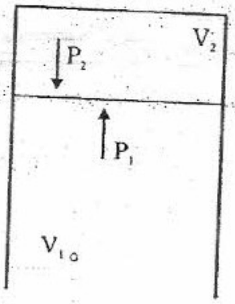
∴ $$\oint w = w_1 + w_2$$

$$= -P_2\left(V_2 - V_1\right) - P_1\left(V_1 - V_2\right)$$

$$= -P_2\left(V_2 - V_1\right) + P_1\left(V_2 - V_1\right)$$

$$\oint W = \left(V_2 - V_1\right) + \left(P_1 - P_2\right)$$

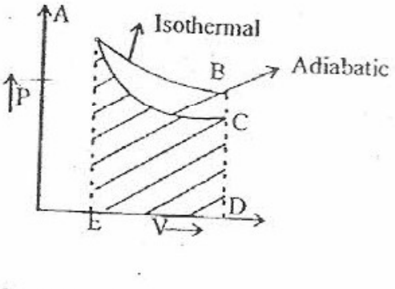
W_{irr} = +ive



Comparison between reversible isothermal & adiabatic expansion of an ideal gas:
Comparison of the Isothermal curve and Adiabatic curve :

It is clear from the curve that the work done in isothermal process is greater than that in adiabatic process is greater than that in adiabatic process since the area (ABDE) under the curve (AB) for the isothermal process is more than the area (ACDE) under the curve (AC) for the adiabatic process.

i.e, $W_{ABDE} = W_{ABC} + W_{ACDE}$
$W_{iso} = W_{ABC} + W_{adia}$



⇒ $\boxed{W_{iso} > W_{adia}}$

Prove that if the final volume of the gas in isothermal and adiabatic process is same, then the final pressure of the gas in isothermal process will be more than that in adiabatic process.

i.e $P_{iso} > P_{adia}$ OR $(P_f)_{iso} > (P_f)_{adia}$

Proof : Let P_i be the initial pressure of the gas in both the process (viz isothermal & adiabatic) & let V_i be the initial volume of the gas in both the processes (viz isothermal and adiabatic. Let V_f be the final volume of the gas in both the processes (viz isothermal and adiabatic). Let P_{iso} be the final pressure of the gas in isothermal process and let P_{aba} be the final pressure of the gas in adiabatic process.

Isothermal Process : For isothermal process, we know that PV= Constant

$$\Rightarrow \quad P_1V_1 = P_2V_2;\ P_iV_i = P_{iso}V_f$$

$$\Rightarrow \quad \boxed{\frac{P_i}{P_{iso}} = \frac{V_f}{V_i}} \qquad \text{... (1)}$$

Adiabatic Process:

For adiabatic Process we know that

PV^γ = constant

$$\Rightarrow \quad P_1V_1^\gamma = P_2V_2^\gamma;\ P_iV_i^\gamma = P_{adia}V_f^\gamma$$

$$\Rightarrow \quad \frac{P_i}{P_{adia}} = \left(\frac{V_f}{V_i}\right)^\gamma \qquad \text{... (2)}$$

From (1) & (2), we have, $\frac{P_i}{P_{adia}} = \left(\frac{P_i}{P_{iso}}\right)^\gamma$ ... (3)

Since $V_f > V_i \Rightarrow \frac{V_f}{V_i} > 1 \Rightarrow \left(\frac{P_i}{P_{iso}}\right) > 1$ & also γ is always greater than 1 (i-e $\gamma > 1$).

Therefore, we have from equation (3)

$$\frac{P_i}{P_{adia}} > \frac{P_i}{P_{iso}};\ \frac{1}{P_{adia}} > \frac{1}{P_{iso}} \qquad [\because P_i > 0]$$

$$\Rightarrow \quad \boxed{P_{iso} > P_{adia}}$$

i.e The final pressure of the gas in isothermal process is more than that in adiabatic process.

*** Prove that if the final pressure of the gas in isothermal and adiabatic process is same, then the final volume of the gas in isothermal process will be more than that in adiabatic process.**

i.e $V_{iso} > V_{adia}$ OR $(V_f)_{iso} > P_{adia}$

In this case also $\boxed{W_{iso} > W_{adia}}$

Let P_i be the initial pressure of the gas in both the processes (viz isothermal and adiabatic) & Let P_f be the final pressure of the gas in both the process (viz isothermal and adiabatic).

Let V_i be the initial volume of the gas in both the processes (viz isothermal and adiabatic).

Let V_{iso} be the final volume of the gas in isothermal process and let V_{adia} be the final volume of the gas in adiabatic process.

Isothermal Process :

For isothermal process, we know that PV= constant

$$\Rightarrow \quad P_1V_1 = P_2V_2;\ P_iV_i = P_fV_{iso}$$

$$\Rightarrow \quad \boxed{\frac{V_{iso}}{V_i} = \frac{P_i}{P_f}} \qquad \text{... (i)}$$

Adiabatic Process: For adiabatic process, we know that

PV^γ = constant

$$\Rightarrow \quad P_1V_1^\gamma = P_2V_2^\gamma;\ P_iV_i^\gamma = P_fV_{adia}^\gamma;\ \left(\frac{V_{adia}}{V_i}\right)^\gamma = \frac{P_i}{P_f};\ \frac{V_{adia}}{V_i} = \left(\frac{P_i}{P_f}\right)^{\frac{1}{\gamma}}$$

From (i) & (ii), we have $\frac{V_{adia}}{V_i} = \left(\frac{V_{iso}}{V_i}\right)^{\frac{1}{\gamma}}$

Taking log on both the sides, we get

$$\log_{10}\left(\frac{V_{adia}}{V_i}\right)=\frac{1}{\gamma}\log_{10}\left(\frac{V_{iso}}{V_i}\right);\ \log_{10}\left(\frac{V_{iso}}{V_i}\right)=\gamma\log_{10}\left(\frac{V_{adia}}{V_i}\right) \qquad \text{... (iii)}$$

Now since, $V_{iso} > V_i \quad \Rightarrow \quad \frac{V_{iso}}{V_i} > 1 \Rightarrow \log\left(\frac{V_{iso}}{V_i}\right) > 0$

And $\quad V_{adia} > V_i \quad \Rightarrow \quad \frac{V_{adia}}{V_i} > 1 \Rightarrow \log\left(\frac{V_{adia}}{V_i}\right) > 0$

And $\boxed{\text{Also, } \gamma > 1}$

Therefore it is clear from the Equation (iii)

$$\log\left(\frac{V_{iso}}{V_i}\right) > \log\left(\frac{V_{adia}}{V_i}\right);\ \frac{V_{iso}}{V_i} > \frac{V_{adia}}{V_i}$$

$\Rightarrow \quad \boxed{V_{iso} > V_{adia}} \qquad [\because V_i > 0]$

i.e The final volume of the gas in isothermal process is more than that in adiabatic process.

Combined Result of (6), (7), (8) & (9)

$$\boxed{(\text{Slope})_{adiabatic} = \gamma(\text{Slope})_{isothermal}}$$

$$\boxed{W_{isothermal} > W_{adiabatic}}$$

When final volume of the gas in same in both the process (viz isothermal and adiabatic), Then

$$\boxed{(P_{final})_{isothermal} > (P_{final})_{adiabatic}}$$

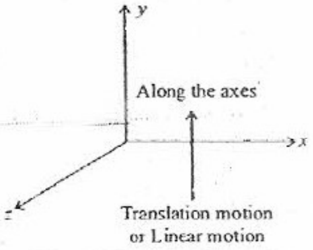
When final pressure of the gas is same in both the processes (viz isothermal and adiabatic), then

$$\boxed{(V_{final})_{isothermal} > (V_{final})_{adiabatic}}$$

Degree of freedom:

It is the number of independent variables coordinates required to specify a molecule in the space or it is the kind of energies sustained by a molecule or by knowing the value of which we can predict about the kind of motion (viz translational, rotational and vibrational) executed by a molecule.

Both kind of molecules (linear and non linear) show three kinds of translational motion (i.e along x, y & z axes).



Non-linear molecules (like NO_2, SO_2, SO_3, CH_4 etc) show three kinds of Rotational motion

Linear molecules (like CO, CO_2, N_2, O_2 etc) show two kinds of rotational motion.

If there are N number of atoms, then the total degree of freedom (DOF) in the space = 3N i.e. Translational degree of freedom + rotational degree of freedom + vibrational degree of freedom= 3N

$\Rightarrow \quad \boxed{N_{tr} + N_{rot} + N_{Vib} = 3N} \qquad \text{... (1)}$

For both kind of molecules (i.e linear & non-linear)

$N_{tr} = 3$

$\therefore \quad (1) \Rightarrow 3 + N_{rot} + N_{Vib} = 3N$

$\Rightarrow \quad \boxed{N_{Vib} = 3N - (3 + N_{rot})} \qquad \text{... (2)}$

For Linear Molecule: $N_{rot} = 2$

$\therefore$ (2) $\Rightarrow N_{Vib} = 3N - (3 + 2) \Rightarrow \boxed{N_{Vib} = 3N-5}$

For non-linear molecular: $N_{rot} = 3$

$\therefore$ (2) $\Rightarrow N_{Vib} = 3N - (3 + 3) \Rightarrow \boxed{N_{Vib} = 3N-6}$

Problem: Calculate N_{Vib} for the following moleculer NO_2, SO_2, CO, SO_3, CO_2, CH_4, N_2, O_2,

Soln. Here linear molcules are CO, CO_2, N_2, O_2. For these molecule $\boxed{N_{Vib} = 3N-5}$

(i) CO

Here N = 2 $\quad \therefore N_{Vib} = 3\times2-5 = 1$

(ii) CO_2

Here N = 3 $\quad \therefore N_{Vib} = 3\times3-5 = 4$

(iii) N_2

Here N = 2 $\quad \therefore N_{Vib} = 3\times2-5 = 1$

(iv) O_2

Here N = 2 $\quad \therefore N_{Vib} = 3\times2-5=1$

And non-linear moleculer are

NO_2, SO_2, SO_3, CH_4,

For these non-linear moleculer, N_{Vib} is given as $N_{Vib} = 3N - 6$

(i) NO_2

Here N = 3 $\quad \therefore N_{Vib} = 3\times3-6 = 3$

(ii) SO_2

Here N = 3 $\quad \therefore N_{Vib} = 3\times3-6 = 3$

(iii) SO_3

Here N = 4 $\quad \therefore N_{Vib} = 3\times4-6 = 6$

(iv) CH_4 $\quad$ Here N = 5 $\quad \therefore N_{Vib} = 3\times5-6 = 9$

Relation between C_V and Degree of Freedom(f):

If the degree of freedom of one molecule is f, then the degree of freedom of N molecules will be Nf.

Now from the equipartition theorem of energy, Average internal energy per degree of feedom per molecule is given as $\varepsilon = \frac{1}{2}kT$ $\quad$ Where, k = Boltzman constant

$$\Rightarrow \quad k = \frac{R}{N} = \frac{8.314\ J/Kmol}{6.023\times10^{23}\ mol^{-1}};\ k = 1.38\times10^{-23}\ J\ K^{-1}$$

Average internal energy of all kind of molecules (i.e of N molecules)

$$E = \frac{1}{2}NfkT;\ E = \frac{1}{2}RfT$$

Now we know that $C_V = \left(\frac{\partial Q}{\partial T}\right)_V;\ C_V = \left(\frac{\partial E}{\partial T}\right)_V$

$[\therefore \partial Q = \partial E + \partial W = \partial E + P\partial V = \partial E + O = \partial E]$

$(\because V = \text{Constant})$ $\qquad (\therefore dV = 0)$

$$\Rightarrow \quad C_V = \left[\frac{\partial}{\partial T}\left(\frac{1}{2}RfT\right)\right]_V;\ C_V = \frac{1}{2}Rf\left(\frac{\partial T}{\partial T}\right)_V;\ C_V = \frac{1}{2}Rf\times1;\ \boxed{C_V = \frac{Rf}{2}}$$

According to the principle of equipartition of energy

Degree of freedom	Symbol	Contribution to C_V
Translational	N_{tr}	$\frac{R}{2}$
Rotational	N_{rot}	$\frac{R}{2}$
Vibrational	N_{Vib}	$\begin{cases} R, \text{At high Temp} \\ 0.2R, \text{At Room Temp} \end{cases}$

i.e. at room temperature the contribution to C_V from N_{vib} is only 20%

$\therefore$ Contribution to C_V from N_{Vib} $= R \times \frac{20}{100} = 0.2\,R$

At high temperature, $(C_V)_{total} = N_{tr}(R/2) + N_{rot}(R/2) + N_{Vib}(R)$

At room temperature, $(C_V)_{total} = N_{tr}(R/2) + N_{rot}(R/2) + N_{Vib}(0.2R)$

At higher temp.	$(C_V)_{Total} = N_{tr}\left(\frac{R}{2}\right) + N_{rot}\left(\frac{R}{2}\right) + N_{Vib}(R)$
At room temp.	$(C_V)_{Total} = N_{tr}\left(\frac{R}{2}\right) + N_{rot}\left(\frac{R}{2}\right) + N_{Vib}(0.20R)$

Problem: Estimate γ at room temperature for

(a) He (b) CH_4

Assuming these gases as ideal gases. What will be the value of γ at higher temperature?

Soln : **Case-I: At room temperature**

(a) He Helium consists of one atom only and atoms have only translation motion.

$\therefore$ $N_{tr} = 3,\ N_{rot} = 0,\ N_{Vib} = 0$

$\therefore$ $(C_V)_{total} = N_{tr}\left(\frac{R}{2}\right) + N_{rot}\left(\frac{R}{2}\right) + N_{vib}(0.20R)$; $(C_V)_{total} = 3 \times \frac{R}{2} + 0 + 0$

$\Rightarrow$ $C_V = \frac{3R}{2}$ & $C_P = C_V + R = \frac{3}{2}R + R = \frac{5}{2}R$

$\therefore$ $\gamma = \frac{C_P}{C_V} = \frac{(5/2)R}{(3/2)R} = \frac{5}{3} = 1.66$

(b) CH_4 it is a non linear molecule

Here $N_{tr} = 3,\ N_{rot} = 3,\ \&\ N = 5$

$\therefore$ $N_{vib} = 3N - 6;\ N_{vib} = 3 \times 5 - 6;\ N_{vib} = 9$

$\therefore$ $(C_V) = N_{tr}(R/2) + N_{rot}(R/2) + N_{vib}(0.20R)$

$\Rightarrow$ $C_V = 3\frac{R}{2} + \frac{3R}{2} + 9 \times 0.20\,R;\ C_V = 3\,R + 1.80\,R;\ C_V = 4.80\,R$

$\Rightarrow$ $C_V = 4.80 \times 8.314\ \frac{J}{K\,mol} = 39.9072$ J/K. mol

$\therefore$ $C_P = C_V + R = (39.9072 + 8.3140) = 48.2212$ J/K; $\gamma = \frac{C_P}{C_V} = \frac{48.2212}{39.9072}$

1.2083

Or $C_P = C_V + R = 4.80\,R + R = 5.80\,R$

$\gamma = \frac{C_P}{C_V} = \frac{5.80R}{4.80R} = 1.2083$ Ans

Case-II: At high temperature:

(a) **He :** Same Value

Helium consists of atom only and atoms have only translation motion

$\therefore$ $N_{tr} = 3, N_{rot} = 0 \;\&\; N_{vib} = 0$

$$\therefore \quad (C_V)_{total} = N_{tr}\left(\frac{R}{2}\right) + N_{rot}\left(\frac{R}{2}\right) + N_{vib}(R);\; C_V = 3 \times \frac{R}{2} + 0 + 0;\; C_V = \frac{3R}{2}$$

$$\Rightarrow \quad C_V = C_V + R = \frac{3}{2}R + R = \frac{5}{2}R$$

$$\therefore \quad \gamma = \frac{C_P}{C_V} = \frac{(5/2)R}{(3/2)R} = \frac{5}{3} = 1.66$$

(b) CH_4 It is a non-linear mosecule

Here $N_{tr} = 3, N_{rot} = 3, N = 5$

$\therefore$ $N_{vib} = 3N - 6 = 3 \times 5 - 6;\; N_{vib} = 9$

$$\therefore \quad (C_V)_{total} = N_{tr}\left(\frac{R}{2}\right) + N_{rot}\left(\frac{R}{2}\right) + N_{vib}(R);\; C_V = \frac{3R}{2} + \frac{3R}{2} + 9R;\; C_V = 3R + 9R;\; C_V = 12R$$

$\therefore$ $C_P = C_V + R = 12R + R = 13R$

$$\therefore \quad \gamma = \frac{C_P}{C_V} = \frac{13R}{12R} = 1.08$$

On the basis of this question, we can say that

On increasing temp C_p, C_V increases. But gamma decreases

Problem: Show that $C_V = \dfrac{R}{\gamma - 1}$ & $C_P = \left(\dfrac{\gamma}{\gamma - 1}\right)R$:

Soln. $C_P - C_V = R;\; \dfrac{C_P}{C_V} - 1 = \dfrac{R}{C_V};\; \gamma - 1 = \dfrac{R}{C_V}$ $\quad\therefore\quad$ $C_V = \left(\dfrac{R}{\gamma - 1}\right)$

Again, $C_P - \dfrac{R}{\gamma - 1} = R;\; C_P = R + \dfrac{R}{\gamma - 1} = R\left(1 + \dfrac{1}{\gamma - 1}\right) = R\left(\dfrac{\gamma - 1 + 1}{\gamma - 1}\right)$

$$\boxed{C_P = R\left(\frac{\gamma}{\gamma - 1}\right)}$$

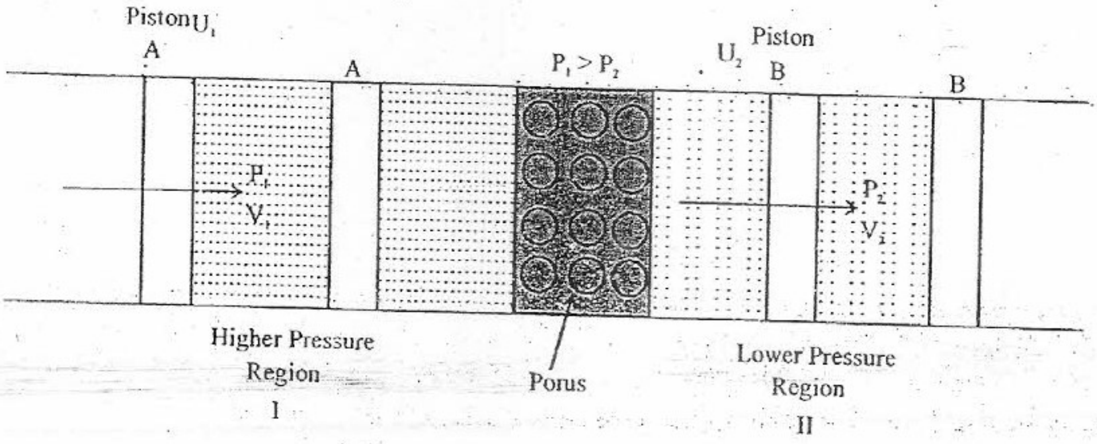
Proved.

JOULE - THOMSON EFFECT

Porus Plug Experiment:

When any gas is subjected from a higher pressure region to a lower pressure region through a porus plug adiabatically, cooling takes place except for H_2 and He. At the same conditions of temp and pressure when these gases are subjected from a higher pressure region to a lower pressure region through a porus plug adiabatically, heating takes place.

This effect is known as 'Joule-Thomson effect'. It is an isoenthalpic and adiabatic process.



Since Joule-Thomson effects is an adiabatic Process, therefore,

$dQ = dU + dW$

$\Rightarrow \quad 0 = dU + dW; -dW = dU \qquad \ldots (1)$

i.e. the work done by the gas is equal to the change in internal energy.

$\Rightarrow \quad -PdV = dU$

$\Rightarrow \quad -P(V_2 - V_1) = U_2 - U_1$

$\Rightarrow \quad -PV_2 + PV_1 = U_2 - U_1$

$\Rightarrow \quad U_1 + PV_1 = U_2 + PU_2$

$\Rightarrow \quad H_1 = H_2$

$\Rightarrow \quad H_2 - H_1 = 0; dH = 0$

$\Rightarrow \quad \Delta H = 0; dH = 0$

$H = \text{constant}$

$\Rightarrow$ Joule-Thomson effect is an isoenthalpic process

Joule Thomson Coefficient:

$$H = H(T, P); \; dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP$$

$$\Rightarrow \quad 0 = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP \qquad [\because \text{In Joule-Thomson effect } dH = 0]$$

$$\Rightarrow \quad 0 = C_P\, dT + \left(\frac{\partial H}{\partial P}\right)_T dP; \; C_P\, dT = -\left(\frac{\partial H}{\partial P}\right)_T dP; \; \left(\frac{dT}{\partial P}\right)_H = -\frac{1}{C_P}\left(\frac{\partial H}{\partial P}\right)_T$$

$$\Rightarrow \quad \boxed{\left(\frac{dT}{dP}\right)_H = -\frac{1}{C_P}\left(\frac{dH}{dP}\right)_T}$$

$\left(\frac{\partial T}{\partial P}\right)_H$ is known as Joule-Thomson coefficient & is denoted by μ_{JT} Joule-Thomson effect (Joule Thomson Coefficient)

$$\mu_{J.T} = -\frac{1}{C_P}\left(\frac{\partial H}{\partial P}\right)_T \quad \ldots (1)$$

From thermodynamic square.

$$dH = TdS + VdP$$

$$\therefore \quad \left(\frac{\partial H}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T + V\left(\frac{\partial P}{\partial P}\right)_T$$

Again, $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$

$$\therefore \quad \mu_{J.T} = -\frac{1}{C_P}\left[-T\left(\frac{\partial V}{\partial T}\right)_P + V\right]$$

$$\boxed{\mu_{J.T} = \frac{1}{C_P}\left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right]} \checkmark \quad \ldots (2)$$

Problem: Show that for ideal gas, $\mu_{J.T} = 0$

$$\because \quad \mu_{J.T} = \frac{1}{C_P}\left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right] = \frac{1}{C_P}\left[T\left(\frac{\partial}{\partial T}\frac{RT}{P}\right)_P - V\right] = \frac{1}{C_P}\left[\frac{R}{P}T\left(\frac{\partial T}{\partial T}\right)_P - V\right]$$

$$= \left[\frac{T}{C_P}\frac{R}{P} - V\right] = \frac{V}{C_P} - V = \frac{1}{C_P}(V - V)$$

$\therefore \quad \boxed{\mu_{J.T} = 0}$ for ideal gas

Problem: Show that for real gas $\mu_{J.T} = \frac{1}{C_P}\left[\frac{2a}{RT} - b\right]$

Soln. $$\mu_{J.T} = \frac{1}{C_P}\left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right] \quad \ldots (1)$$

We have to find value of $\left(\frac{\partial V}{\partial T}\right)_P$ for real gas & put it into above equation.

$$\frac{\partial}{\partial T}\left[\overset{\text{I}}{\left(P + \frac{a}{V^2}\right)}\overset{\text{II}}{(V - b)}\right]_P = \frac{\partial}{\partial T}(\overset{\text{I}}{R}\ \overset{\text{II}}{T})_P$$

$$\left(P + \frac{a}{V^2}\right)\frac{\partial}{\partial T}(V - b)_P + (V - b)\frac{\partial}{\partial T}\left(P + \frac{a}{V^2}\right)_P = R\left(\frac{\partial T}{\partial T}\right)_P + T\left(\frac{\partial R}{\partial T}\right)_P$$

$$\left(P + \frac{a}{V^2}\right)\left(\frac{\partial V}{\partial T}\right)_P - \left(\frac{\partial b}{\partial T}\right)_P + (V - b)\left[\left(\frac{\partial P}{\partial T}\right)_P + \left(\frac{\partial}{\partial T}\frac{a}{V^2}\right)_P = R\right.$$

$$\left(P + \frac{a}{V^2}\right)\left[\left(\frac{\partial V}{\partial T}\right)_P - \left(\frac{\partial b}{\partial T}\right)_P\right] + (V - b)\left[\left(\frac{\partial P}{\partial T}\right)_P + \left(\frac{\partial a}{\partial T V^2}\right)_P\right] = R$$

$$\left(P + \frac{a}{V^2}\right)\left[\left(\frac{\partial V}{\partial T}\right)_P - 0\right] + (V - b)\left[0 + \frac{-2a}{V^3}\left(\frac{\partial V}{\partial T}\right)_P\right] = R$$

$$\left(P+\frac{a}{V^2}\right)\left(\frac{\partial V}{\partial T}\right)_P+(V-b)-\frac{2a}{V^3}\left(\frac{\partial V}{\partial T}\right)_P ; \left(\frac{\partial V}{\partial T}\right)_P\left[\left(P+\frac{a}{V^2}\right)-\frac{2a}{V^3}(V-b)\right]=R$$

$$\left(\frac{\partial V}{\partial T}\right)_P\left[\left(\frac{RT}{(V-b)}\right)-\frac{2a}{V^3}(V-b)\right]=R ; \left(\frac{\partial V}{\partial T}\right)_P\left[\frac{RT}{V-b}-\frac{2a(V-b)}{V^3}\right]=R \qquad \left(P+\frac{a}{V^2}\right)=\frac{RT}{(V-b)}$$

$$\left(\frac{\partial V}{\partial T}\right)_P=\frac{R}{\frac{RT}{(V-b)}\left[1-\frac{2a(V-b)^2}{V^3RT}\right]} \qquad \dots(2)$$

Putting value of equation (2) in equation (1)

$$\mu_{J.T}=\frac{1}{C_P}\left[\frac{TR}{\frac{RT}{V-b}\left[1-\frac{2aV^2}{V^3RT}\right]}-V\right]=\frac{1}{C_P}\left[V+\frac{2av}{RTV}-b-\underset{\underset{\text{neglected}}{\downarrow}}{\frac{2ab}{RTV}}-V\right] \qquad [V-b=V]$$

$$\mu_{J.T}=\frac{1}{C_P}\left[(V-b)\left(1-\frac{2a}{RTV}\right)^{-1}-V\right]$$

$$\left[\text{so,}\left(1-\frac{2a}{RTV}\right)^{-1}=1+\frac{2a}{RTV}\right] \qquad \left(\frac{2ab}{RTV}\text{ is very small may be neglected}\right)$$

$$\boxed{\mu_{J.T}=\frac{1}{C_P}\left[\frac{2a}{RT}-b\right]}$$

Inversion temperature (T_i):

The temp. at which $\mu_{J.T}$ becomes zero i.e. neither heating nor cooling takes place & gas behaves ideally is called inversion temperature.

$$\mu_{J.T}=\left(\frac{\partial T}{\partial P}\right)_H=\frac{1}{C_P}\left[\frac{2a}{RT}-b\right]$$

If $\mu_{J.T}=0$, $T=T_i$

$$0=\frac{1}{C_P}\left[\frac{2a}{RT_i}-b\right]; \frac{2a}{RT_i}-b=0 ; \frac{2a}{RT_i}=b$$

$$\boxed{T_i=\frac{2a}{Rb}} \qquad \dots(3)$$

Now following experimental condition indicates heating or cooling.
During J.T. effect.

$dP = -\text{ive}$ $\quad\therefore\quad$ $\mu_{J.T}=\left(\frac{\partial T}{\partial P}\right)_H$

1. If $\mu_{J.T}$ = positive then ∂T should be negative, $T_2 < T_1$
Thus cooling takes place.

In experimental condition:

$$\mu_{J.T} = \frac{1}{C_p}\left[\frac{2a}{RT} - b\right] \qquad \text{If } \mu_{J.T} = +\text{ve} \quad \text{means } \mu_{J.T} > 0$$

$$0 < \frac{1}{C_p}\left[\frac{2a}{RT} - b\right]; \left(\frac{2a}{RT} - b\right) > 0; \left(\frac{2a}{RT} - b\right) > 0; \frac{2a}{Rb} > T$$

$$\boxed{T_i > T}$$

Thus experimental temperature should be lesser than the inversion temperature of a gas for cooling.

2. **If $\mu_{J.T}$ = negative:**

Thus ∂T should be positive

$\therefore \quad T_2 - T_1 > 0; T_2 > T_1$ (heating takes place)

In experiemental condition:

$$0 > \frac{1}{C_p}\left[\frac{2a}{RT} - b\right]; \frac{2a}{RT} < b; \frac{2a}{Rb} < T; T_i < T \qquad [T = \text{experimental temp.}]$$

If experimetnal temperature is greater than T_i heating takes during J.T. experiement.

Note: H_2 & He gases have a very low T_i (–80°C & –240°C). This temperature is always below the experiemental condition temperature, thus heating happen.

Problem: Show that $T_i = \frac{1}{\alpha_i}$ for ideal gas.

Soln. $\mu_{J.T} = \frac{1}{C_p}\left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right]$

(If $T = T_i$) than $\mu_{J.T}$ becomes zero.

$$0 = \frac{1}{C_p}\left[T_i\left(\frac{\partial V}{\partial T}\right)_P - V\right]; T_i\left(\frac{\partial V}{\partial T}\right)_P = V; \quad T_i = \frac{V}{\left(\frac{\partial V}{\partial T}\right)_P} = \frac{1}{\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P} = \frac{1}{\alpha_i}$$

$$\boxed{T_i = \frac{1}{\alpha_i}} \qquad \text{proved.}$$

Note: (1) Isothermal J.T. coefficient (ϕ)

$$(\phi) = \left(\frac{\partial H}{\partial P}\right)_T$$

(2) Isoenthalpic J.T. coefficient (μ)

$$\mu = \left(\frac{\partial T}{\partial P}\right)_H \qquad \because \qquad \mu_{J.T} = -\frac{1}{C_p}\left(\frac{\partial H}{\partial P}\right)_T; \boxed{\mu_{J.T} = -\frac{1}{C_p}\phi}$$

Calculation of various thermodynamic relation for vander waal's relation:

1. **Expression of W:**

$$dw = -p_{ext}.dv$$

For reversible change in volume, $P_{ext} = P_{int} \pm dP \simeq P_{int}$

$$\therefore \quad dw = -P_{int}\,dv; \quad \int dw = -\int_{V_1}^{V_2}\left(\frac{nRT}{V - nb} - \frac{n^2a}{V^2}\right)dV$$

$$\boxed{W = -nRT\,\ell n\frac{V_2 - nb}{V_1 - nb} - n^2a\left(\frac{1}{V_2} - \frac{1}{V_1}\right)}$$

2. **Expressed for ΔU :**

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$$

For vander waal gas $\left(\frac{\partial P}{\partial T}\right)_V = \frac{nR}{V - nb}$

$$\therefore \quad \left(\frac{\partial U}{\partial V}\right)_T = \frac{nRT}{V - nb} - P = \frac{nRT}{(V - nb)} - \left(\frac{nRT}{(V - nb)} - \frac{n^2a}{V^2}\right) = \frac{n^2a}{V^2};\ \left(\frac{\partial U}{\partial V}\right)_T = \frac{n^2a}{V^2}$$

$$\because \quad U = f(T, V)$$

$$\therefore \quad dU = \left(\frac{\partial U}{\partial V}\right)_V .dT + \left(\frac{\partial U}{\partial T}\right)_V .dV$$

For Isothermal change $dT = 0$

$$\therefore \quad dU = \left(\frac{\partial U}{\partial V}\right)_T .dV;\ \int dU = \int_{V_1}^{V_2} \frac{n^2a}{V^2} dV;\ \boxed{\Delta U = -n^2a\left(\frac{1}{V^2} - \frac{1}{V_1}\right)}$$

Similarly, $q = \Delta U - w$; $\boxed{q = nRT\ell n\frac{V_2 - nb}{V_1 - nb}}$

3. **Expression for ΔH :**

$$\because \quad \Delta H = \Delta U + \Delta(PV)$$

$$\Delta H = -n^2a\left(\frac{1}{V_2} - \frac{1}{V_1}\right) + \Delta\left[\left(\frac{nRT}{V - nb} - \frac{n^2a}{V^2}\right)V\right]$$

$$= -n^2a\left(\frac{1}{V_2} - \frac{1}{V_1}\right) + nRT\left(\frac{V_2}{V_2 - nb} - \frac{V_1}{V_1 - nb}\right) - n^2a\left(\frac{1}{V_2} - \frac{1}{V_1}\right)$$

$$\boxed{\Delta H = -2n^2a\left(\frac{1}{V_2} - \frac{1}{V_1}\right) + nRT\left(\frac{V_2}{(V_2 - nb)} - \frac{V_1}{(V_1 - nb)}\right)}$$

Carnot cycle/Carnot reversible heat engine:

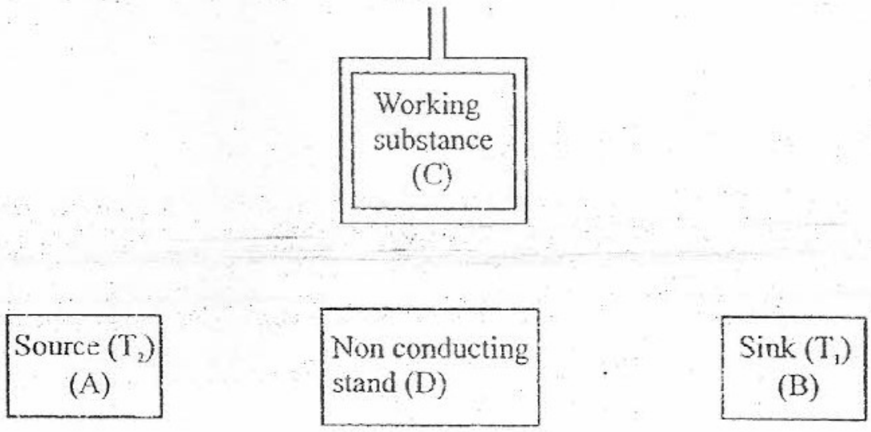
The carnot cycle is a hypothetical, ideal & reversible cyclic process, devised by a french engineer Sadi Carnot (1824), to demonstrate the maximum convertibility of heat into work. An ideal machine to demonstrate this cycle is called carnot heat engine.

The work done in a carnot cycle is maximum because the various steps involved are reversible & the reversible work is the maximum possible work which a system can do.

Carnot heat engine is ideal and regarded as standard (ideal) by which the performance of an actual heat engine is compared.

Schematic plan: It consist of

1. Source of heat (A), at high temperature T_2.
2. Sink (B) ,at lower temperature T_1
3. Working substance (C)
4. Perfect heat insulating stand (D)

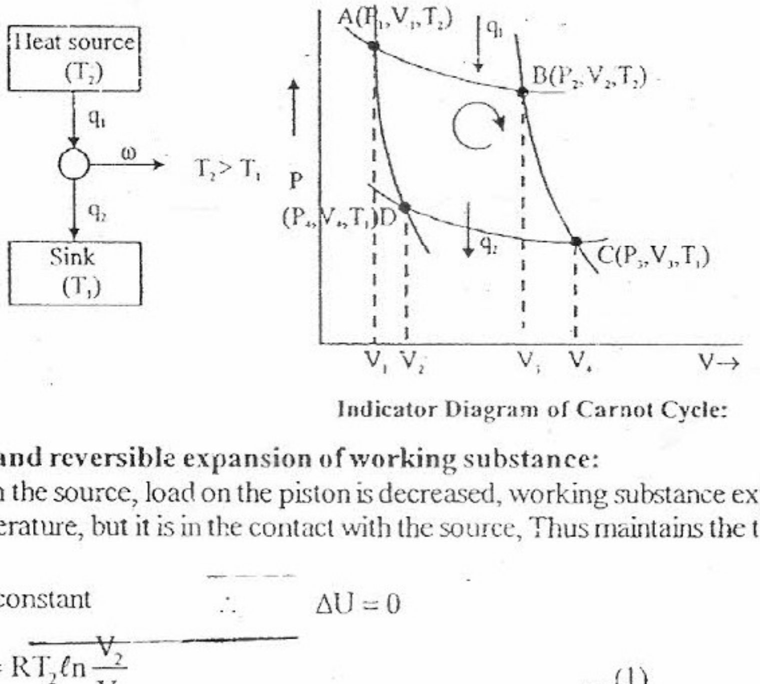


[It is conducting & heat capacity very large]

[It is conducting & heat capacity very large]

The ideal carnot's cycle is the cycle in which working substance is an ideal gas.

Operations involved in Carnot cycle: This cycle involves four operations. These are as follows.



Indicator Diagram of Carnot Cycle:

Step 1: Isothermal and reversible expansion of working substance:

Cyclinder is placed on the source, load on the piston is decreased, working substance expands, external work happens. Fall in temperature, but it is in the contact with the source, Thus maintains the temp. quantity of heat absorbed is q_1.

$$T_2 = \text{constant} \qquad \therefore \qquad \Delta U = 0$$

First law, $q_1 = -w_1 = RT_2 \ln \frac{V_2}{V_1}$ ...(1)

Step 2: Adiabatic reversible expansion of working substance:
Cylinder is removed from the source put on the perfectly insulating pad. Load is further decreased to cause expansion of working substance adiabatically.

$\therefore \quad q = 0 \qquad$ From first law

$$w_2 = \Delta U = C_V\left(T_1 - T_2\right) \qquad \text{... (2)}$$

Step 3: Isothermal and reversible compression of substance:
Cylinder is again transfer to the sink at temperature (T_1), load on the piston is slowly increased. Gas is compressed. Heat developed passes into the sink. Temperature remain constant at T_1.

$$q_2 = -w_3 = RT_1 \ell n \frac{V_4}{V_3} \qquad \text{... (3)}$$

Step 4: Adiabatic reversible compression of substance:
Cylinder is again transfer to the insulating pad. Load on the piston is again slightly increased, so that substance undergo slow adiabatic compression. Temp. rises from $T_1 \rightarrow T_2$

$$w_4 = C_V\left(T_2 - T_1\right) \qquad \text{... (4)}$$

Thus net work during one complete cycle.

$$W_{Total} = w_1 + w_2 + w_3 + w_4 = -RT_2 \ell n \frac{V_2}{V_1} + C_V\left(T_1 - T_2\right) - RT_1 \ell n \frac{V_4}{V_3} + C_V\left(T_2 - T_1\right)$$

But $C_V\left(T_1 - T_2\right) = -C_V\left(T_2 - T_1\right)$

$$\therefore \quad \boxed{W_{Total} = -RT_2 \ell n \frac{V_2}{V_1} - RT_1 \ell n \frac{V_4}{V_3}} \qquad \text{... (5)}$$

Now for adiabatic curve BC & DA

$$TV^{\gamma-1} = \text{Constant}$$

for curve BC, $T_2 V_2^{\gamma-1} = T_1 V_3^{\gamma-1}$

$$\therefore \quad \frac{T_1}{T_2} = \left(\frac{V_2}{V_3}\right)^{\gamma-1} \qquad \text{... (6)}$$

for curve DA, $T_1 V_4^{\gamma-1} = T_2 V_1^{\gamma-1}$

$$\therefore \quad \frac{T_1}{T_2} = \left(\frac{V_1}{V_4}\right)^{\gamma-1} \qquad \text{... (7)}$$

from equation (6) & (7)

$$\left(\frac{V_2}{V_3}\right)^{\gamma-1} = \left(\frac{V_1}{V_4}\right)^{\gamma-1}; \; \frac{V_2}{V_3} = \frac{V_1}{V_4} \qquad \therefore \quad \boxed{\frac{V_2}{V_1} = \frac{V_3}{V_4}} \qquad \text{... (8)}$$

Putting value of equation (8) in equation (5)

$$W_{Total} = -RT_2 \ell n \frac{V_2}{V_1} - RT_1 \ell n \frac{V_1}{V_2} = -RT_2 \ell n \frac{V_2}{V_1} + RT_1 \ell n \frac{V_2}{V_1}$$

$$\boxed{W_{Total} = -R \ell n \frac{V_2}{V_1}\left(T_2 - T_1\right)} \qquad \text{... (9)}$$

Efficiency (η) of carnot heat engine: The ratio of work done by the system to the amount of heat transferred to the system at the higher temperature.

$$\eta = \frac{-W_{Total}}{q_2} = \frac{q_2 + q_1}{q_2} = 1 + \frac{q_1}{q_2}$$

Absorbed heat $q_1 = RT_2 \ell n \frac{V_2}{V_1}$ $\quad \therefore \quad \eta = \frac{-w}{q_1} = \frac{-\left[-R\ell n \frac{V_2}{V_1}(T_2 - T_1)\right]}{RT_2 \ell n \frac{V_2}{V_1}}$

$$\eta = \frac{T_2 - T_1}{T_2}; \quad \boxed{\eta = 1 - \frac{T_1}{T_2}} \quad \checkmark \qquad \ldots (10)$$

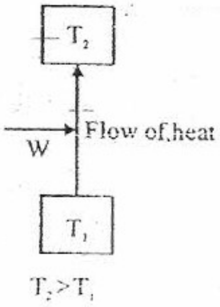
Discussion of above equation (10):

1. η does not depend on the working substance used.
2. η depends only on the ratio of sink to source temp.
3. η is always less than one.
4. η is one only when $\frac{T_1}{T_2}$ is zero. i.e. when $T_1 = 0K(-273°C)$ or $T_2 = \infty$. Both these temp. are impossible to obtain. Therefore, it is impossible to construct a heat engine whose efficiency is unity or 100%. That is heat can't be transformed completely into work.
5. For all reversible cycle operating between the same initial & final temperature, the efficiency is the same.

Refrigerator:

Energy will not flow spontaneously from a low temperature to a high temperature without any work. Refrigerator does this work. Refrigerator is a machine operates in a manner opposite to that of a heat engine. Working substance take heat from the low temp. source then same work is performed on it & finally it rejects heat to a high temp. source. Space to the refrigerated is the low temp. source & surrounding atmosphere is high temp. source.

In carnot engine heat is input work is output. In refrigerator heat is output & work is input.



Coefficient of performance (β):

The ratio of heat transferred from a lower temperature to a higher temperature to the work done on the machine to cause this removal, i.e. $\beta = \frac{|q_C|}{w}$

The less the work done the more efficient the operation and greater the coefficient of performance.

$\because \quad w_{irr} > w_{rev} \quad \therefore \quad \beta_{rev} > \beta_{irr}$

$$\beta = \frac{|q_C|}{|q_h| - |q_C|} = \frac{T_1}{T_2 - T_1}$$

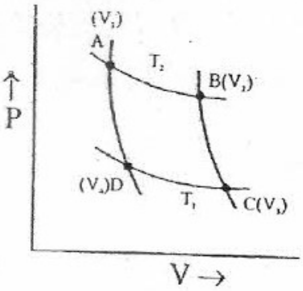
At $T_1 \to 0$ kelvin $\quad \beta = 0$

$$\therefore \quad w = \frac{|q_C|}{\beta} = \frac{(q_C)}{0} = \infty$$

Thus as the temperature of a system is lowered the amount of work required to lower the temperature further increases rapidly and approaches infinity as the zero kelvin temperature is attained.

Efficiency in the form of expansion ration (ρ)/Adiabatic expansion ratio:

$$\boxed{\rho = \frac{V_3}{V_2} = \frac{V_4}{V_1}}$$



efficiency $(\eta) = 1 - \frac{T_1}{T_2}$

for adiabatic curve $TV^{\gamma-1}$

$$\therefore \quad T_2 V_2^{(\gamma-1)} = T_1 V_3^{(\gamma-1)}$$

$$\frac{T_1}{T_2} = \left(\frac{V_2}{V_3}\right)^{\gamma-1}; \quad \frac{T_1}{T_2} = \frac{1}{\left(\frac{V_2}{V_3}\right)^{\gamma-1}} = \frac{1}{(\rho)^{\gamma-1}} \quad \therefore \quad \boxed{\eta = 1 - \left(\frac{1}{\rho}\right)^{\gamma-1}}$$

Relation between (η) & (β):

$$\because \quad \beta = \frac{T_1}{T_2 - T_1} \qquad T_2 > T_1$$

Again $\eta = \frac{T_2 - T_1}{T_2}$; $\frac{1}{\eta} = \frac{T_2}{T_2 - T_1}$; $\frac{1}{\eta} - 1 = \frac{T_2}{T_2 - T_1} - 1$, $\frac{1-\eta}{\eta} = \frac{T_2 - T_2 + 1}{T_2 - T_1} = \frac{T_1}{T_2 - T_1}$

$$\boxed{\beta = \frac{1-\eta}{\eta}}$$

$$\eta = \frac{T_1 - T_2}{T_2}, \quad \beta = \frac{T_2}{T_1 - T}$$

$$\beta = \frac{1-\eta}{\eta}$$

Again, $\eta\beta = 1 - \eta$; $\eta\beta + \eta = 1$; $\eta = \frac{1}{\beta + 1}$

Problem: What % of T_1 of T_2 for a 10% efficiency?

Soln. $\eta = 1 - \frac{T_1}{T_2}$; $\frac{10}{100} = 1 - \frac{T_1}{T_2}$; $\frac{T_1}{T_2} = 1 - \frac{10}{100} = \frac{90}{100} = 0.9$

$T_1 = .9T_2$; $T_1\% = .9T_2 \times 100$; $\boxed{T_1\% = 90\% T_2}$

Problem: For an ideal gas during adiabatic reversible expansion plot of log P versus log V is linear. What will be the slope?

Soln. $PV^\gamma = \text{constant}$

$\log P + \gamma \log V = C$

$\log P = -\gamma \log V + C$

$y \quad = \quad mx + C$

$\therefore \quad \boxed{\text{slope}(m) = -\gamma}$

Problem : In a carnot engine 200 cal heat is given to the sink by a reservoir at 27°C. If temp. of the source is 57°C, then find:

(i) How much heat flows from the source.

(ii) Efficiency of the engine

(iii) Work done by the reservoir.

Soln : Here, given, $Q_2 = 200$ cal, $Q_1 = ?$

$T_2 = 27°\text{C} = (27 + 273) = 300\text{K}$

$T_1 = 57°\text{C} = (57 + 273) = 330\text{K}$; $\eta = ?$ & $W = ?$

(i) We have, $\frac{Q_1}{T_1} = \frac{Q_2}{T_2}$

$\Rightarrow \quad \frac{Q_1}{330K} = \frac{200cal}{300K}; \frac{Q_1}{11} = \frac{200}{10} cal; Q_1 = 220 \, cal$

(ii) $\eta = 1 - \frac{Q_2}{Q_1}; \eta = 1 - \frac{200}{220}; \eta = 1 - \frac{10}{11}; \eta = \frac{1}{11}$

(iii) $W = Q_1 - Q_2 = (220 - 200)cal = 20cal$

OR

(ii) $\eta = 1 - \frac{T_2}{T_1} = 1 - \frac{300}{330} = 1 - \frac{10}{11} = \frac{1}{11}$

(i) $\eta = 1 - \frac{Q_2}{Q_1}; \frac{1}{11} = 1 - \frac{200}{Q_1}; 1 - \frac{1}{11} = \frac{200}{Q_1}; \frac{10}{11} = \frac{200}{Q_1}; Q_1 = 220cal$

(iii) $W = Q_1 - Q_2 = (220 - 200)cal = 20cal$

Problem: Temperature of the sink of a carnot engine is 7°C and efficiency is 50%, then calculate change in temperature of the source to increase the efficiency of the same engine 70%.

Soln. We know that $\eta = 1 - \frac{T_{sink}}{T_{source}}$ ...(i)

Case-I: $\eta = 50\% = \frac{50}{100} = \frac{1}{2}; T_{sink} = 7°C = (7 + 273) \, K = 280K \quad \therefore (i) \quad \frac{1}{2} = 1 - \frac{280K}{T_{source}}$

$\frac{280K}{T_{source}} = 1 - \frac{1}{2} = \frac{1}{2}; T_{source} = 560K$

Case-II: $\eta = 70\% = \frac{70}{100} = \frac{7}{10}; T_{sink} = 7°C = (7 + 273) \, K = 280K$

$\therefore \quad (i)' \quad \Rightarrow \quad \frac{7}{10} = 1 - \frac{280K}{T_{source}}; \frac{280K}{T_{source}} = 1 - \frac{7}{10} = \frac{3}{10}; T_{source} = \frac{280K \times 10}{3 \times 1}; T_{source} = 933.33K$

$\Rightarrow$ Change in temperature of the source = (933.33 − 560)K = 373.33K

Problem: The efficiency of a carnot's cycle is 1/6. If on reducing the temperature of the sink by 75K, efficiency becomes $\frac{1}{3}$, then find initial and final temperature between which the cycle is working.

Soln: We have, $\eta = 1 - \frac{T_2}{T_1}; \frac{1}{6} = 1 - \frac{T_2}{T_1}; \frac{T_2}{T_1} = 1 - \frac{1}{6}; \frac{T_2}{T_1} = \frac{5}{6}$

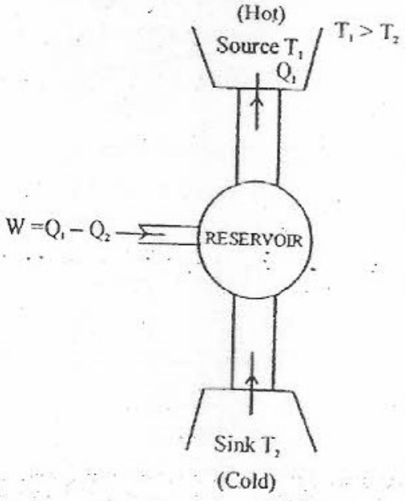
Now, $\eta = 1 - \frac{T_2 - 75}{T_1}; \frac{1}{3} = 1 - \frac{T_2}{T_1} + \frac{75}{T_1}; \frac{1}{3} = 1 - \frac{5}{6} + \frac{75}{T_1}$ [Using equation (i)]

$\Rightarrow \quad \frac{1}{3} = \frac{1}{6} + \frac{75}{T_1}; \frac{75}{T_1} = \frac{1}{3} - \frac{1}{6}; \frac{75}{T_1} = \frac{1}{6}; T_1 = 450 \, k$

(ii) $\Rightarrow T_2 = \frac{5}{6} \times 450 \, K = 5 \times 75 \, K = 375 \, K$

Problem: A carnot refrigerator takes heat from water 0°C and discard it to a room at 27°C. 1kg of water at 0°C is to be changed into ice at 0°C. How many calories of heat is discarded to the room? What is the work done by the refrigerator? In this process what is the value of cop?

Soln:



Here $T_1 = 27°C = 300K$, $T_2 = 0°C = 273K$

1kg 0°C Water → 0°C ice

$$\therefore \quad Q_2 = 1 \times 10^3\ \text{g} \times 80\ \frac{\text{Cal}}{\text{g}};\ Q_2 = 8 \times 10^4\ \text{Cal}$$

We have, $\frac{Q_1}{Q_2} = \frac{T_1}{T_2}$; $Q_1 = Q_2 \times \frac{T_1}{T_2}$; $Q_1 = 8 \times 10^4\ \text{cal} \times \frac{300}{273}$

$$\therefore \quad \text{Work done} = Q_1 - Q_2 = 8 \times 10^4 \times \frac{300}{273}\ \text{Cal} - 8 \times 10^4\ \text{Cal} = 8 \times 10^4 \times \left[\frac{300}{273} - 1\right]\ \text{Cal}$$

$$= 8 \times 10^4 \times \left[\frac{27}{273}\right]\ \text{Cal} = \frac{72}{91} \times 10^4\ \text{Cal} = 0.79 \times 10^4\ \text{Cal}$$

$$\text{and} \quad \text{Cop} = \frac{Q_2}{Q_1 - Q_2} = \frac{8 \times 10^4\,\text{Cal}}{8 \times 10^4\left[\frac{300}{273} - 1\right]\text{Cal}} = \frac{273}{27} = \frac{91}{9} \approx 10$$

Problem: Show that $\eta_{rev} > \eta_{irr}$

Soln. Let us have 2 cycle one operating reversibly and other irreversibly. Let both operates between the same temperature and involve perfect gas as the working substance.

Step 1: Isothermal expansion:

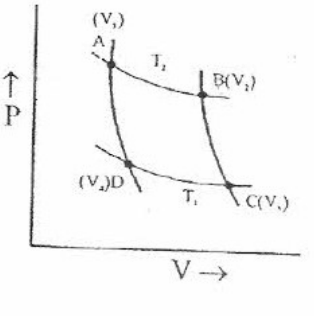
$$V_1 \to V_2$$

$$-w_{2(rev)} = q_{2(rev)} = RT_2 \ell n \frac{V_2}{V_1}$$

$$-w_{2(irr)} = q_{2(irr)} = P_{ext}\left(V_2 - V_1\right)$$

$$\because \quad w_{2(rev)} > w_{2(irr)}$$

$$\therefore \quad q_{2(rev)} > q_{2(irr)}$$



Step 2: Isothermal compression:

$$V_3 \to V_4;\ -w_1(\text{rev}) = q_1(\text{rev}) = RT_1 \ell n \frac{V_4}{V_3};\ -w_1(\text{irr}) = q_1(\text{irr}) = P_{ext}(V_4 - V_3)$$

$\because$ $w_1(\text{irr}) > w_1(\text{rev});\ q_1(\text{irr}) > q_1(\text{rev})$

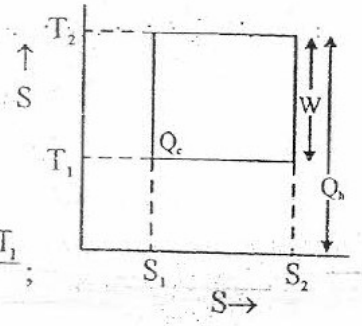
$$\eta_{rev} = 1 - \frac{q_{1(rev)}}{q_2(\text{rev})};\ \eta_{irr} = 1 - \frac{q_{1(irr)}}{q_{2\ (irr)}} \qquad \because \quad \frac{q_{1(rev)}}{q_{2(rev)}} < \frac{q_{1(irr)}}{q_{2(irr)}}$$

$\therefore$ $\boxed{\eta_{rev} > \eta_{irr}}$ **Proved.**

T—S diagram of carnot cycle:

Total heat taken by system $dQ = TdS$

$$Q = T_2(S_2 - S_1)$$



Heat energy converted into work $-w = dQ = (T_2 - T_1)(S_2 - S_1)$

$$\therefore \quad \eta = \frac{-w}{Q} = \frac{(T_2 - T_1)(S_2 - S_1)}{T_2(S_2 - S_1)} = \frac{T_2 - T_1}{T_2};$$

$$\boxed{\eta = 1 - \frac{T_1}{T_2}}$$

$$\boxed{\eta = 1 - \frac{T_{sink}}{T_{soure}}}$$

$$\boxed{\frac{T_{sink}}{Q_{rejeet}} = \frac{T_{soure}}{Q_{absorber\ given}}}$$

SECOND LAW OF THERMODYNAMICS

Statement of the Second Law of Thermodynamics :

1. "Heat cannot spontaneously pass from a colder to a warmer body." (R.J.E calusius).
2. "It is impossible to transfer heat from a colder system to a warmer without other simultaneous changes occurring in the two systems, or in their environment." (P.S. Epstein)
3. "Every system which is left to itself will, on the average, change toward a condition of maximum probability." (G.N. Lewis).
4. "The state of maximum entropy is the most stable state for an isolated system." (Enrico Fermi)
5. "In any irreversible process the total entropy of all bodies concerned is increased." (G.N. Lewis)
6. "In an adiabatic process the entropy either increases or remains unchanged.

   $$\Delta S \geq 0$$

   where the singn (>) referes to the irreversible, the (=) to the reversible case (P.S. Epstein).
7. "The entropy function of a system of bodies tends to increase in all physical and chemical processes occurring in nature, if we include in the system all such bodies which are affected by the change." (Saha)
8. "The entropy increases towards a maximum and the energy of the universe is constant." (R.J.E. Clausius)
9. "Gain in information is loss in entropy." (G.N. Lewis)
10. "Entropy is times arrow." (A Eddington)
11. "Every system left to itself changes rapidly or slowly in such a way to approach a definite final state or rest. No system of its own will change away from the state of equilibrium, except through the influence of external agencies". (G.N. Lewis).
12. "There is a general tendency in nature for energy to pass from more available to less available forms." (J.A.V. Butter)
13. "When an actual process occurs it is impossible to invent a means of restoring every system concerned to its original condition." (G.N. Lewis)
14. "Work can always be completely converted into heat but heat can't be completely converted into work without leaving a permanent change in the system or surroundings. Only a fraction of heat can be converted into useful work & the rest remains unavailable & unconverted.

Entropy and unavailable energy:

In the carnot cycle working between two temperatures T_2(source) & T_1(sink). If q_2 is heat absorbed from source at T_2 & q_1 be the heat rejected to the sink at T_1, then work done is given by

$-w = q_2 - q_1$ =energy available for doing useful work

∴ q_1 = unavailable portion of heat i.e. unavailable energy

$$\eta = 1 - \frac{q_1}{q_2} = 1 - \frac{T_1}{T_2} \qquad \therefore \quad \frac{q_1}{q_2} = \frac{T_1}{T_2} \qquad \therefore \quad \frac{q_1}{T_1} = \frac{q_2}{T_2}$$

$$q_1 = \left(\frac{q_2}{T_2}\right).T_1 \qquad \ldots (1)$$

Thus for a given sink (T_1), unavailable energy (q_1) is determined by (q_2/T_2). Hence entropy is unavailable energy of system, i.e. law of increase of entropy for irreversible processes is connected with the law of dissipation of energy. Therefore, the second law of thermodynamics says that entropy is a measure of unavailable energy.

Spontaneous process and non-spontaneous process:

The process which proceed by themselves & bring the system closer to the equilibrium are called spontaneous process. All natural process are spontaneous.

The process which can't proceed by themselves are called non-spontaneous process. These require external force & brings the system away from equilibrium.

⇒ In spontaneous processes entropy of universe is completely increasing i.e. unavailable energy goes on increasing & the workable energy is continuously decreasing. A spontaneous process comes to an end at equilibrium, & since at equilibrium the entropy is maximum, it can be remarked that nature is trying to attain the state of maximum entropy.

⇒ Entropy is a state function

∴ $dS = \frac{dq}{T}$ = an exact differential

⇒ Entropy is an extensive property.

⇒ Entropy of reaction:

$$\Delta S_{(\text{reaction})} = \sum^{\text{Product}} n\,S - \sum^{\text{Reactant}} m\,S$$

S = absolute entropies of respective substances.
n & m = moles of products & reactants respectively

For a reaction, $m_1A + m_2B \longrightarrow n_1C + n_2D$

$$\Delta S_{(\text{reaction})} = \left[n_1S_{(C)} + n_2S_{(D)}\right] - \left[m_1S_{(A)} + m_2S_{(B)}\right]$$

Entropy changes in reversible process:

Let us consider an isothermal reversible process. In this the system absorbs heat q from surroundings at temp. T. This results in an increase in the entropy of system given by.

$$\Delta S_{\text{system}} = \frac{+q}{T}$$

$$\Delta S_{\text{surroundings}} = \frac{-q}{T}$$

Total entropy of the process = $\Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$

$$\Delta S_{\text{process}} = \frac{q}{T} + \left(\frac{-q}{T}\right)$$

∴ $\boxed{\Delta S_{\text{process}} = 0}$ ... (1)

entropy change for Reversible process is zero.

Entropy changes in an irreversible processes:

Let q amount of heat is transferred from system which is at higher temp. (T_2) to the surroundings which is at lower temp. (T_1)

∴ Decrease in entropy of system $= \frac{-q}{T_2}$

Incease in entropy of surroundings $= \frac{+q}{T_1}$

∴ Net entropy change of process $= \Delta S_{\text{system}} + \Delta S_{\text{surrounding}}$

$$\Delta S_{\text{process}} = \frac{-q}{T_2} + \frac{q}{T_1} = q\left[\frac{1}{T_1} - \frac{1}{T_2}\right] = q\left[\frac{T_2 - T_1}{T_1.T_2}\right]$$

∵ $T_2 - T_1 = +\text{ve}$

∴ $\boxed{\Delta S_{\text{process}} = +\text{ve}}$ or $\boxed{\Delta S > 0}$ ... (2)

Combining equation (1) & (2)

$\boxed{\Delta S_{\text{process}} \geq 0}$

⇒ **Adiabatic processes are isoentropic:**

∵ $dS = \frac{dq}{T}$

For adiabatic process $dq = 0$

$\therefore \quad \boxed{dS = 0}$ or $S = \text{constant}$

Entropy - change during phase-transitions: (Phase different temp. same)

$$\boxed{\Delta S_{Trans} = \frac{\Delta H_{trans}}{T_{trans}}}$$

ΔS_{tans} = entropy change for phase transformation process.

ΔH_{trans} = enthalpy change for phase transition at constant pressure & constant temperature.

T_{rans} = phase transition temperature

1. **Melting:**

$$A_{(S)} \overset{T_f}{\rightleftharpoons} A(\ell) \qquad \boxed{\Delta S_{fusion} = \frac{\Delta H_{fusion}}{T_{fusion}}}$$

2. **Vaporisation:**

$$A_{(\ell)} \overset{T_b}{\rightleftharpoons} A_{(V)} \quad \therefore \quad \boxed{\Delta S_{vap} = \frac{\Delta H_{vap}}{T_b}} \qquad [T_b = \text{boiling point}]$$

3. **Sublimation:**

$$A_{(S)} \rightleftharpoons A_{(vap)}; \ \Delta S_{subli} = \frac{\Delta H_{subli}}{T_{subli}}$$

4. **Allotropic transformation:**

$$\text{Solid}(\alpha) \rightleftharpoons \text{Solid}(\beta)$$

α & β are two allotropic form of a solid.

$$\boxed{\Delta S_{trans} = \frac{\Delta H_{trans}}{T_{trans}}}$$

Combination of first and second law:

For a reversible process

(i) According to first law, $dq = dE + PdV$

(ii) According to second law, $dS = \frac{dq}{T}$

From these two, $dS = \frac{dE + PdV}{T}$

$$\boxed{TdS = dE + PdV} \qquad \dots (1)$$

Entropy change for ideal gas in different cases:

Change in entropy for an ideal gas in different cases:

We know that, change in entorpy is given as $\Delta S = \int \frac{dQ}{T}$; $\Delta S = \int \frac{dU + dW}{T}$

$$\Rightarrow \quad \Delta S = \int \frac{dU + PdV}{T} \qquad [\because dQ = dU + dW \text{ (1st law of T.D)}] \ [\because dW = PdV]$$

$$\Rightarrow \quad \Delta S = \int \frac{nC_V dT + PdV}{T}; \ \Delta S = \int nC_V \frac{dT}{T} + \int \frac{PdV}{T} \qquad [\because dU = nC_V dT]$$

$$\Rightarrow \quad \Delta S = nC_V \int \frac{dT}{T} + \int \frac{nR\,dV}{V} \qquad [\because PV = nRT \Rightarrow \frac{P}{T} = \frac{nR}{V}]$$

$$\Rightarrow \quad \Delta S = nC_V\int_{T_1}^{T_2}\frac{dT}{T} + nR\int_{V_1}^{V_2}\frac{dU}{V}\ ;\ \Delta S = nC_V[\ln T]_{T_1}^{T_2} + nR\,[\ln V]_{V_1}^{V_2}$$

$$\Rightarrow \quad \boxed{\Delta S = nC_V\ln\left(\frac{T_2}{T_1}\right) + nR\ln\left(\frac{V_2}{V_1}\right)} \qquad \text{...(i)}$$

This is the genral expression for the change in entropy for an ideal gas when temp. & volume (i.e. T& V) vary.

(i) Isothermal Process: In isothermal Process T = constt

$$\Rightarrow \quad T_1 = T_2 = T \qquad \Rightarrow \qquad \ln\left(\frac{T_2}{T_1}\right) = \ln(1) = 0$$

$$(i) \Rightarrow \quad \boxed{\Delta S_{\text{isothermal}} = nR\ln\left(\frac{V_2}{V_1}\right)}$$

(ii) Isochoric Process: In isochoric process

$$V = \text{Constt} \quad \Rightarrow \quad V_1 = V_2 = V$$

$$\Rightarrow \quad \Delta S_{\text{isochoric}} = n\,C_V\ln\left(\frac{T_2}{T_1}\right) + n\,R\ln\left(\frac{V}{V}\right)$$

$$\Rightarrow \quad \Delta S_{\text{isochoric}} = n\,C_V\ln\left(\frac{T_2}{T_1}\right) + n\,R\ln\ln 1;\ \Delta S_{\text{isochoric}} = nC_V\ln\left(\frac{T_2}{T_1}\right) + n\,R\ln\left(\frac{V}{V}\right)$$

$$\Rightarrow \quad \Delta S_{\text{isochoric}} = n\,C_V\ln\left(\frac{T_2}{T_1}\right) + 0 \qquad \boxed{\Delta S_{\text{isochoric}} = n\,C_V\ln\left(\frac{T_2}{T_1}\right)}$$

Now, Ideal gas Equation is

$$PV = n\,RT$$

$$\Rightarrow \qquad P_1V_1 = n\,RT_1 \qquad \text{... (ii)}$$

$$\& \qquad P_2V_2 = n\,RT_2 \qquad \text{... (iii)}$$

$$\frac{(iii)}{(ii)} \Rightarrow \qquad \frac{T_2}{T_1} = \frac{P_2V_2}{P_1V_1}$$

Now making substitution in equation (i), we get

$$\Delta S = n\,CV\ln\left(\frac{P_2}{P_1}\cdot\frac{V_2}{V_1}\right) + nR\ln\left(\frac{V_2}{V_1}\right);\ \Delta S = n\,C_V\ln\left(\frac{P_2}{P_1}\right) + nC_V\ln\left(\frac{V_2}{V_1}\right) + n\,R\ln\left(\frac{V_2}{V_1}\right)$$

$$\Rightarrow \quad \Delta S = n\,C_V\ln\left(\frac{P_2}{P_1}\right) + n(C_V + R)\ln\left(\frac{V_2}{V_1}\right)$$

$$\Rightarrow \quad \boxed{\Delta S = n\,C_V\ln\left(\frac{P_2}{P_1}\right) + n\,C_P\ln\left(\frac{V_2}{V_1}\right)} \quad (\because\ C_P - C_V = R)$$

This is the general express for the change in entropy for an ideal gas when pressure and volume (P&V) vary.

(iii) Isobaric process : In isobaric process

$$P = \text{constant}$$

$$\Rightarrow \qquad P_1 = P_2 = P$$

$$\therefore (iv) \Rightarrow \quad \Delta S_{\text{isobaric}} = n\,C_V\ln\left(\frac{P}{P}\right) + n\,C_P\ln\left(\frac{V_2}{V_1}\right);\ \Delta S_{\text{isobaric}} = n\,C_V\ln 1 + n\,C_P\ln\left(\frac{V_2}{V_1}\right)$$

$$\Rightarrow \quad \Delta S_{\text{isobaric}} = 0 + n\,C_P\ln\left(\frac{V_2}{V_1}\right) \qquad \boxed{\Delta S_{\text{isobaric}} = n\,C_P\ln\left(\frac{V_2}{V_1}\right)}$$

(iv) Adiabatic Process: In adiabatic process, Q= constant

$$\Rightarrow \quad dQ = 0;\ \Delta S_{\text{adiabatic}} = \int \frac{dQ}{T} \quad \Rightarrow \quad \boxed{\Delta S_{\text{adiabatic}} = 0};\ S_2 - S_1 = 0;\ S_1 = S_2$$

i.e. Adiabatic process is an isoentropic process.

$$\boxed{H_2O_{(ice)} \xrightarrow[\text{or Fusion}]{\text{Melting}} H_2O(l)}$$

Change in entropy in this process is given as

$$\Delta S_{\text{fusion}} = \frac{\Delta H_{\text{fusion}}}{T_{\text{fusion}}} = \frac{mL_{\text{fusion}}}{T_{\text{fusion}}}$$

Where, ΔH_{fusion} = Heat of fusion
L_{fusion} = latent heat of fusion of ice (which is here absorbed)
T_{fusion} = Temperature for fusion

$$\boxed{H_2O(l)_{(ice)} \xrightarrow{\text{Freezing}} H_2O(ice)}$$

Change in intropy in this process is given as

$$\Delta S_{\text{freezing}} = -\frac{\Delta H_{\text{freezing}}}{T_{\text{freezing}}} = -\frac{mL_{\text{freezing}}}{T_{\text{freezing}}}$$

Where, $\Delta H_{\text{freezing}}$ = Heat of freezing
T_{freezing} = Temperature for freezing
L_{freezing} = latent heat of freezing of ice (which is here given out)

$$\boxed{H_2O(\ell) \xrightarrow{\text{vaporisation}} H_2O_{(\text{Vapour})}}$$

Change in entropy in this process is given as

$$\Delta S_{\text{Vapour}} = \frac{\Delta H_V}{T_V} = \frac{mL_V}{T_V}$$

Where, ΔH_V = Heat of vapourisation
L_V = latent heat of vapourisation of water
T_V = Temperature for vapourisation

Specific heat capacity of water=1 Cal / g / °C; 1 Cal / g / K
Specific heat capacity of ice=0.5 Cal / g / °C; 0.5 Cal / g /K
Latent heat of vapour=540 Cal / g
Latent heat of ice=80 Cal / g

Problem: 20g of vapour at 100°C is being condensed into water and then it is converted into ice at –40°C. Then calculate total change in entropy of the process.

Soln: $\Delta S_2 = \int \frac{dQ_2}{T} = \int_{T_1}^{T_2} \frac{ms\,dT}{T} = ms \int_{T_1}^{T_2} \frac{dT}{T}$

$$\Rightarrow \quad \Delta S_2 = ms \ln\left(\frac{T_2}{T_1}\right) \quad \text{... (i)}$$

$$100^\circ \text{ Vapour} \xrightarrow[Q_1]{\Delta S_1} 100^\circ\text{C Water} \xrightarrow[Q_2]{\Delta S_2} 0^\circ\text{C Water} \xrightarrow[Q_3]{\Delta S_3} 0^\circ\text{C Ice} \xrightarrow[Q_4]{\Delta S_4} 40^\circ\text{C Ice}$$

We have, $\Delta S_1 = -\frac{mL}{T}$; $\Delta S_1 = -\frac{(20g) \times 540\ (\text{Cal/g})}{(100+273)\ K}$; $\Delta S_1 = -\frac{10800}{373}$ Cal/K

$$\Rightarrow \quad \Delta S_1 = -28.9544 \text{ Cal/K}$$

Now, $\Delta S_2 = \frac{(20g) \times (1\text{Cal/gK})}{1} \ln\left[\frac{0+273)K}{(100+273)K}\right]$

$\Rightarrow \quad \Delta S_2 = 20 \ln\left(\frac{273}{373}\right) \text{Cal/K}; \ \Delta S_2 = 20 \times 2.303 \times \log_{10}\left(\frac{273}{373}\right) \text{Cal/K}$

$\Rightarrow \quad \Delta S_2 = 46.06 \times \log_{10}(0.7319) \text{ Cal/K}$

$\Rightarrow \quad \Delta S_2 = 46.06 \times (-0.1355) \text{ Cal/K}$

$\Rightarrow \quad \Delta S_2 = -6.2411 \text{Cal/K}$

$\Rightarrow \quad \Delta S_3 = -\frac{(20g)\times 80\,(\text{Cal/g})}{(0+273)K}; \ \Delta S_3 = -\frac{1600}{273} \text{ Cal/K}; \ \Delta S_3 = -5.8608 \text{ Cal/K}$

Now, $\Delta S_4 = \int \frac{dQ_4}{T} = \int_{T_1}^{T_2} \frac{ms\,dT}{T}; \ \Delta S_4 = ms \int_{T_1}^{T_2} \frac{dT}{T}; \ \Delta S_4 = ms \ln\frac{T_2}{T_1}$

$\Rightarrow \quad \Delta S_4 = (20g) \times \left(0.5 \frac{\text{Cal}}{gK}\right) \times \ln\left[\frac{(-40+273)}{(0+273)K}\right]; \ \Delta S_4 = 10 \ln\left(\frac{233}{273}\right) \text{Cal/K}$

$\Rightarrow \quad \Delta S_4 = 2.303 \times 10 \log_{10}\left(\frac{233}{273}\right) \text{Cal/K}; \ \Delta S_4 = 23.03 \times \log_{10}(0.8535) \text{ Cal/K}$

$\Rightarrow \quad \Delta S_4 = 23.03 \times [-0.0688] \text{ Cal/K}; \ \Delta S_4 = -1.5845 \text{ Cal/K}$

$\therefore$ Total change in entroy (ΔS) is given as

$\Rightarrow \quad \Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3 + \Delta S_4$

$\Rightarrow \quad \Delta S = -[28.9544 + 6.2411 + 5.8608 + 1.5845] \text{ Cal/K}$

$\Rightarrow \quad \Delta S = -42.6408 \text{ cal/K}$

Problem : 10g ice at –80°C is being converted into vapour at 100°C then calculate total change in entropy.

Soln : $\Delta S_1 = \int \frac{dQ_1}{T} = \int_{T_1}^{T_2} \frac{ms\,dT}{T} = ms \int_{T_1}^{T_2} \frac{dT}{T}; \ \Delta S_1 = ms \ln\left(\frac{T_2}{T_1}\right); \ \Delta S_1 = ms \ln\left(\frac{T_2}{T_1}\right)$

$\Rightarrow \quad \Delta S_1 = (10g) \times \left(0.5 \frac{\text{Cal}}{g\,K}\right) \ln\left[\frac{(0+273)K}{(-80+273)K}\right]; \ \Delta S_1 = 5 \ln\left(\frac{273}{193}\right) \text{ Cal/K}$

$$\boxed{\begin{matrix}-80^\circ \text{ Ice} \\ (10\text{ g})\end{matrix}} \xrightarrow[\Delta S_1]{Q_1} \boxed{0^\circ\text{C Ice}} \xrightarrow[Q_2]{\Delta S_2} \boxed{0^\circ\text{C Water}} \xrightarrow[Q_3]{\Delta S_3} \boxed{100^\circ\text{C Water}} \xrightarrow[Q_4]{\Delta S_4} \boxed{100^\circ\text{C Vapour}}$$

$\Rightarrow \quad \Delta S_1 = 5 \times 2.303 \log_{10}\left(\frac{273}{193}\right) \text{ Cal/K}; \ \Delta S_1 = 11.515 \log_{10}(1.4145) \text{ Cal/K}$

$\Rightarrow \quad \Delta S_1 = 11.515 \times 0.1506 \text{ Cal/K}; \ \Delta S_1 = 1.73\,42 \text{ Cal/K}$

Now, $\Delta S_2 = \frac{(10g)\times(80 \text{ Cal/g})}{(0+273)\text{K}} = \frac{800}{273} \text{ Cal/K}; \ \Delta S_2 = 2.934 \text{ Cal/K}$

Now, $\Delta S_3 = \int \frac{dQ}{T} = \int_{T_1}^{T_2} \frac{ms\,dT}{T} = ms \int_{T_1}^{T_2} \frac{dT}{T} \ ; \Delta S_3 = ms \ln\left(\frac{T_2}{T_1}\right)$

$\Rightarrow \quad \Delta S_3 = (\log) \times \left(1 \frac{\text{Cal}}{g\,K}\right) \times \ln\left[\frac{(100+273)K}{(0+273)K}\right]; \ \Delta S_3 = 10 \ln\left(\frac{373}{273}\right) \text{ Cal/K}$

$\Rightarrow \quad \Delta S_3 = 2.303 \times 10 \times \log_{10}\left(\frac{373}{273}\right) \text{ Cal/K}; \ \Delta S_3 = 23.03 \times \log_{10}(1.3663) \text{ Cal/K}$

$\Rightarrow \quad \Delta S_3 = 23.03 \times 0.1355 \text{ Cal/K}; \ \Delta S_3 = 3.1206 \text{ Cal/K}$

Now, $\Delta S_4 = \frac{(10g)\times(540 \text{ Cal/g})}{(100+273)\text{K}}; \ \Delta S_4 = \frac{5400}{373} \text{ Cal/K}$

$\Rightarrow$ $\Delta S_4 = 14.4772$ Cal/K

$\therefore$ Total change in entropy ΔS is given as

$$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3 + \Delta S_4$$

$\Rightarrow$ $\Delta S = (1.7342 + 2.9304 + 31206 + 14.4772)$ Cal/K

$\Rightarrow$ $\Delta S = 22.2624$ Cal/K

Problem: 2g of a liquid A having specific heat capacity (C_A=0.7 Cal/g/K) at 40°C is mixed with 3g of another liquid B having specific heat capacity (C_B = 0.3 cal/g/K) at 20°C then calcualte total change in entropy of the entire process.

Soln: Let T_{mixo} be the temperatrue of the resultant liquid after mixing.

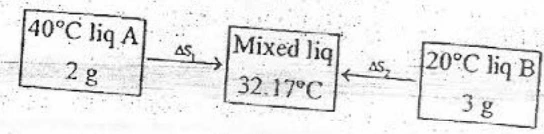
Now from the 1st principle of calorimetry, we a have

Heat given ≡ Heat taken

$$(2g) \times \left(0.7\frac{Cal}{g°C}\right) \times (40°C - T_{mix}) = (3g) \times \left(0.3\frac{Cal}{g°C}\right)(T_{mix} - 20°C)$$

$$1.4 \times (40°C - T_{mix}) = 0.9\,(T_{mix} - 20°C);\ 56 - 1.4\,T_{mix} = 0.9\,T_{mix} - 18$$

$\Rightarrow$ $2.3\,T_{mix} = 74;\ T_{mix} = 32.17°C$



We have, $\Delta S_1 = \int \frac{dQ}{T} = \int_{T_1}^{T_2} \frac{msdT}{T} = ms\int_{T_1}^{T_2}\frac{dT}{T};\ \Delta S_1 = ms\ln\left(\frac{T_2}{T_1}\right)$

$\Rightarrow$ $\Delta S_1 = (2g) \times \left(\frac{0.7\ Cal}{g\ K}\right)\ln\left[\frac{(32.17+273)K}{(40+273)K}\right];\ \Delta S_1 = 1.4 \times \ln\left(\frac{305.17}{313}\right)$ Cal /K

$\Rightarrow$ $\Delta S_1 = 1.4 \times \ln(0.97498)$ Cal/K; $\Delta S_1 = 1.4 \times 2.303 \times \log_{10}(0.9750)$ Cal/K

$\Rightarrow$ $\Delta S_1 = 3.2242 \times [-0.011]$ Cal/K

$\Rightarrow$ $\Delta S_1 = -0.0355$ Cal/K

Now $\Rightarrow$ $\Delta S_2 = \int \frac{dQ}{T} = \int_{T_1}^{T_2} \frac{msdT}{T} = ms\int_{T_1}^{T_2}\frac{dT}{T};\ \Delta S_2 = ms\ln\left(\frac{T_2}{T_1}\right)$

$\Rightarrow$ $\Delta S_2 = (3g) \times \left(\frac{0.3\ Cal}{g\ k}\right)\ln\left[\frac{(32.17+273)k}{(20+273)k}\right];\ \Delta S_2 = 1.9 \times \ln\left(\frac{305.17}{293}\right)$ Cal /K

$\Rightarrow$ $\Delta S_2 = 0.9 \times \ln(1.0415)$ Cal/K; $\Delta S_2 = 0.9 \times 2.303 \times \log_{10}(1.0415)$ Cal/K

$\Rightarrow$ $\Delta S_2 = 2.0727 \times 0.0176$ Cal/K

$\Rightarrow$ $\Delta S_2 = 0.0365$ Cal/K

$\therefore$ Total Change in entropy (ΔS) in given as

$\Delta S = \Delta S_1 + \Delta S_2,\ \Delta S = (-0.0355 + 0.0365)$ Cal/K

$\Rightarrow$ $\Delta S = 0.0010$ Cal/K

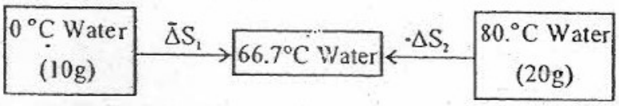
Problem: 10 g of water at 40°C is mixed with 20 g of water at 80°C. Then calculate the total change in entropy of the entire process.

Let T_{mix} be the temperature of water after mixing. Now, From the 1st principle of calorimetry, we have

Heat given ≡ Heat taken

$\Rightarrow$ $(20g) \times \left(\frac{1Cal}{g\ °C}\right) \times (80°C - T_{mix}) = (10g) \times \left(\frac{1Cal}{g\ °C}\right)(T_{mix} - 40°C)$

$\Rightarrow$ $1600°C - 20\,T_{mix} = 10\,T_{mix} - 400°C;\ 30\,T_{mix} = 2000°C;\ T_{mix} = 66.7°C$



We have, $\Delta S_1 = \int\frac{dQ}{T} = \int_{T_1}^{T_2}\frac{msdT}{T} = ms\int_{T_1}^{T_2}\frac{dT}{T}$; $\Delta S_1 = ms\ln\left(\frac{T_2}{T_1}\right)$

⇒ $\Delta S_1 = (10g)\times\left(\frac{1Cal}{g\,K}\right)\ln\left[\frac{(66.7+273)K}{(40+273)K}\right]$; $\Delta S_1 = 10\times\ln\left(\frac{339.7}{313}\right)$ Cal /K

⇒ $\Delta S_1 = 10\times\ln(1.0853)$ Cal/K; $\Delta S_1 = 2.303\times10\times\log_{10}(1.0853)$ Cal/K

⇒ $\Delta S_1 = 23.03\times10\times\log_{10}(1.0853)$ Cal/K

⇒ $\Delta S_1 = 0.8176$ Cal/K

Now ⇒ $\Delta S_2 = \int\frac{dQ}{T} = \int_{T_1}^{T_2}\frac{msdT}{T} = ms\int_{T_1}^{T_2}\frac{dT}{T}$; $\Delta S_2 = ms\ln\left(\frac{T_2}{T_1}\right)$

⇒ $\Delta S_2 = (3g)\times\left(\frac{1\,Cal}{g\,K}\right)\times\ln\left[\frac{(66.7+273)K}{(80+273)K}\right]$; $\Delta S_2 = 20\times\ln\left(\frac{339}{253}\right)$ Cal /K

⇒ $\Delta S_2 = 20\times\ln(0.9623)$ Cal/K

⇒ $\Delta S_2 = 20\times2.303\times\log_{10}(0.9623)$ Cal/K

⇒ $\Delta S_2 = 46.06\times[-0.0167]$ Cal/K

⇒ $\Delta S_2 = -0.7692$ Cal/K

∴ Total Change in entropy (ΔS) in given as

$\Delta S = \Delta S_1 + \Delta S_2$

⇒ $\Delta S = [0.8176 - 0.7692)$ Cal/K; $\Delta S = 0.0484$ Cal/K

Problem: If 2 g of steam at (100°C) is blown into a calorimeter containing 20 g of water at 20°C. If water equivalent of calorimeter is 10g, Then calculate total entropy change of the entire process.

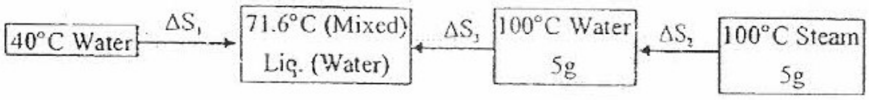
Soln: Let T_{mix} be the temp of the water after steam (100°C) has been condensed into water (20°C) From the 1st principle of calorimetry, we have

Heat given = Heat taken

⇒ $(2g)\times\left\{540\left(\frac{Cal}{g}\right)+(2g)\times\left(\frac{1Cal}{g\,°C}\right)\right\}(100-Tmix)°C = (20+10)\,g\times\left(\frac{1Cal}{g\,°C}\right)(T_{mix}-20)°C$

⇒ $1080 + 200 - 2T_{mix} = 30\,T_{mix} - 600$; $32\,T_{mix} = 1080 + 200 + 600$; $32\,T_{mix} = 1080$

⇒ $T_{mix} = \frac{1880}{32}$; $T_{mix} = 58.75$ °C



We have,

$\Delta S_1 = \int\frac{dQ}{T} = \int_{T_1}^{T_2}\frac{msdT}{T} = ms\int_{T_1}^{T_2}\frac{dT}{T} = ms\ln\frac{T_2}{T_1}$

⇒ $\Delta S_1 = (30g)\times\left(\frac{1Cal}{g\,K}\right)\ln\left[\frac{(58.75+273)K}{(20+273)K}\right]$; $\Delta S_1 = 30\times2.303\times\log_{10}\left[\frac{331.75}{293}\right]$ Cal /K

⇒ $\Delta S_1 = 69.09\times\log_{10}(1.13)$ Cal/K; $\Delta S_1 = 69.09\times0.0531$ Cal/K

⇒ $\Delta S_1 = 3.669$ Cal/K; $\Delta S_1 = 3.669$ Cal/K

Now $\Rightarrow$ $\Delta S_2 = -\dfrac{(2g)\times 540(\text{Cal/g})}{(100+273)\text{K}} = -\dfrac{1080}{373}$ Cal/K; $\Delta S_2 = -2.895$ Cal/K

and $\Rightarrow$ $\Delta S_3 = \int \dfrac{dQ}{T} = \int_{T_1}^{T_2} \dfrac{ms\,dT}{T} = ms\int_{T_1}^{T_2}\dfrac{dT}{T} = \text{ms}\ln\dfrac{T_2}{T_1}$

$$\Rightarrow \quad \Delta S_3 = (2\text{g}) \times \left(\frac{1\text{Cal}}{\text{g K}}\right)\ln\left[\frac{(58.75+273)K}{(100+273)K}\right]$$

$$\Rightarrow \quad \Delta S_3 = 2\times 2.303\times \log_{10}\left[\frac{331.75}{373}\right] \text{Cal /K}$$

$$\Rightarrow \quad \Delta S_3 = 4.606 \times \log_{10}(0.89) \text{ Cal/K}$$

$$\Rightarrow \quad \Delta S_3 = -0.233 \text{ Cal/K}$$

$\therefore$ Total Change in entropy (ΔS) in given as

$$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3$$

$$\Rightarrow \quad \Delta S = (3.669 - 2.895 - 0.233) \text{ Cal/K}$$

$$\Rightarrow \quad \Delta S = (3.669 - 3.128) \text{ Cal/K}$$

$$\Rightarrow \quad \Delta S = 0.541 \text{ Cal/K}$$

Problem: If 5g vapour at 100°C is blown into a calorimetre having 90g water at 40°C & entire vapour get condensed into the water. Then calculate total change in the entropy.

Soln:

Let T_{mix} be the temp of the water after vapour (100°C) has been condensed into water (40°C) Now from the 1st priniciple of calorimetry, we have

Heat given = Heat taken

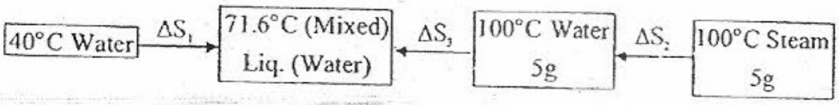
$$(5\text{g})\times 540\left(\frac{\text{Cal}}{\text{g}}\right) + (5g)\times\left(\frac{1\text{Cal}}{\text{g °C}}\right)(100 - T_{mix})°\text{C} = (90\text{ g})\times\left(\frac{1\text{Cal}}{\text{g °C}}\right)(T_{mix} - 40)°\text{C}$$

$$\Rightarrow \quad 2700 + 500 - 5T_{mix} = 90\,T_{mix} - 3600$$

$$\Rightarrow \quad 95\,T_{mix} = 3200 + 3600 = 6800$$

$$\Rightarrow \quad T_{mix} = \frac{6800}{95}$$

$$\Rightarrow \quad T_{mix} = 71.6°\text{C}$$



We have,

$$\Delta S_1 = \int\frac{dQ}{T} = \int_{T_1}^{T_2}\frac{ms\,dT}{T} = ms\int_{T_1}^{T_2}\frac{dT}{T}\,\text{dT}; \Delta S_1 = \text{ms}\ln\left(\frac{T_2}{T_1}\right); \Delta S_1 = (90\text{g})\times\left(\frac{1\text{Cal}}{\text{g K}}\right)\ln\left[\frac{(71.6+273)K}{(40+273)K}\right]$$

$$\Rightarrow \quad \Delta S_1 = 90\times\ln\left[\frac{344.6}{313}\right] \text{Cal /K}; \Delta S_1 = 90\ln(1.1) \text{ Cal/K}$$

$$\Rightarrow \quad \Delta S_1 = 90\times 2.303\log_{10}(1.1) \text{ Cal/K}; \Delta S_1 = 207.27\times 0.0414 \text{ Cal/K}; \Delta S_1 = 8.581 \text{ Cal/K}$$

Now $\Delta S_2 = -\dfrac{(5g)\times(540\text{Cal/g})}{(100+273)\text{K}}$; $\Delta S_2 = -\dfrac{2700}{373}$ Cal/K; $\Delta S_2 = -7.239$ Cal/K

And $\Delta S_3 = \int\dfrac{dQ}{T} = \int_{T_1}^{T_2}\dfrac{ms\,dT}{T} = ms\int_{T_1}^{T_2}\dfrac{dT}{T}$; $\Delta S_3 = \text{ms}\ln\times\left(\dfrac{T_2}{T_1}\right)$

$\Rightarrow \quad \Delta S_3 = (5g) \times \left(\frac{1\text{ Cal}}{g\text{ K}}\right) \times \ln\left[\frac{(71.6+273)K}{(100+273)K}\right]; \Delta S_3 = 5 \times \ln\left(\frac{344.6}{373}\right)$ Cal/k

$\Rightarrow \quad \Delta S_3 = 5 \times 2.303 \times \log_{10}\left(\frac{344.6}{373}\right)$ Cal/K; $\Delta S_3 = 11.515 \times \log_{10}(0.92)$ Cal/K

$\Rightarrow \quad \Delta S_3 = 11.515 \times (-0.0362)$ Cal/K; $\Delta S_3 = -0.417$ Cal/K

$\therefore$ Total Change in entropy (ΔS) in given as

$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3$

$\Rightarrow \quad \Delta S = (8.581 - 7.239 - 0.417)$ Cal/K; $\Delta S = 0.925$ Cal/K

Calculation of ΔS when vander waal gas heated & expanded simultaneously:

Consider n-moles of a vander waal gas. The temperature of gas is changed from T_1 to T_2 & at the same time the volume of gas changes from V_1 to V_2. This process is done at constant external pressure & in reversible manner. Then by first and second law:

$$TdS = dq_{rev} = dE + PdV \qquad \ldots (1)$$

Let $\quad E = f(T,V);\ dE = \left(\frac{\partial E}{\partial T}\right)_V .dT + \left(\frac{\partial E}{\partial V}\right)_T .dV$

$$dE = C_V dT + \left(\frac{\partial E}{\partial V}\right)_T .dV \qquad \ldots (2)$$

from equations (1) & (2)

$$TdS = C_V .dT + \left(\frac{\partial E}{\partial V}\right)_T .dV + PdV$$

$$\therefore \quad dS = C_V\left(\frac{dT}{T}\right) + \frac{1}{T}\left[\left(\frac{\partial E}{\partial V}\right)_T + P\right]dV \qquad \ldots (3)$$

now for n-moles of vander waal gas.

$$\left(P + \frac{n^2a}{V^2}\right)(V - nb) = nRT$$

$$P + \frac{n^2a}{V^2} = \frac{nRT}{(V - nb)} \qquad \ldots (4)$$

Now, $\left(\frac{\partial E}{\partial V}\right)_T$ = internal pressure $\left(\pi = \frac{n^2a}{V^2}\right)$ for real gas.

therefore, from equation (3), we get

$$dS = C_V\left(\frac{dT}{T}\right) + \frac{1}{T}\left[\frac{n^2a}{V^2} + P\right]dV \qquad \ldots (5)$$

from equations (4) and (5)

$$dS = C_V\left(\frac{dT}{T}\right) + \frac{1}{T}\left[\frac{nRT}{(V - nb)}\right]dV$$

$$\boxed{dS = C_V\left(\frac{dT}{T}\right) + \frac{nR}{(V-nb)}dV} \qquad \text{... (6)}$$

Taking C_V as independent of T, integrating equation (6) between suitable limits, we get

$$\Delta S = nC_V\left[\ell nT\right]_{T_1}^{T_2} + nR\left[\ell n(V-nb)\right]_{V_1}^{V_2}$$

$$\Delta S = nC_V \ell n\frac{T_2}{T_1} + nR\ell n\left[\frac{(V_2-nb)}{(V_1-nb)}\right] \qquad \text{... (7)}$$

Cases - I: When it expands isothermally only.

$$\Delta T = 0;\ \boxed{\Delta S_T = nR\ell n\left(\frac{V_2-nb}{V_1-nb}\right)}$$

Case - II: When V is constant:

$$(V_1-nb) = (V_2-nb) \qquad \therefore \qquad \boxed{\Delta S_V = nC_V\ell n\frac{T_2}{T_1}}$$

Criteria for feasibility of a process:

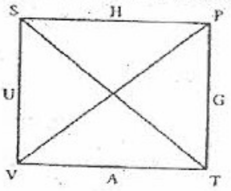
1. All energy change i.e. dH, dG, dA & dU should be -ve or equal to zero for a process to take irreversibly & reversibily respectively. The correct constant can be obtained from thermodynamic square

(a) $(dH)_{S,P} \le 0$

(b) $(dG)_{T,P} \le 0$

(c) $(dA)_{V,T} \le 0$

(d) $(dU)_{S,V} \le 0$



2. For function like dS, the feasibility criteria can be obtained by thermodynamic square.

$dU = TdS - PdV$

$\therefore \quad -dU + TdS - PdV = 0$ for reversible process

& $\quad -dU + TdS - PdV > 0$ for irreversible process.

At constant S & V

$$dS = 0,\ dV = 0 \qquad \therefore \qquad -(dU)_{S,V} \ge 0$$

$$\boxed{(dU)_{S,V} \le 0}$$

Again, from $-dU + TdS - PdV \ge 0$

At constant U & volume (V).

$$dU = 0, \qquad dV = 0 \qquad \therefore \qquad (TdS)_{U,V} \ge 0$$

$$\boxed{(dS)_{U,V} \ge 0}$$

This is the proper criteria for spontanity.

Clausius - Clapeyron Equation:

- This is an important equation for the use of transition state equilibria between two phases of the same substance.

(a) Clausius equation: Change in pressure with respect to change in temp. $\left(\frac{dP}{dT}\right)$ is called Clausius equation.

Derivation of Clausius equation from maxwell's relation:

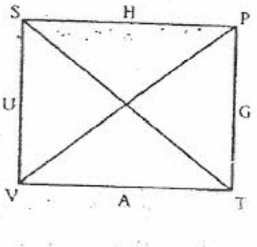
$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$$

multiply above & below by 'T' in R.H.S

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{TdS}{T\partial V}\right)_T$$

or $\frac{dP}{dT} = \frac{TdS}{TdV}$ $[\because TdS = dQ]$

$$\frac{dP}{dT} = \frac{dQ}{T(V_2 - V_1)}$$



This is called Clausius equation.

Derivation of Clausius equation from Gibb's free energy concept:

When a definite amount of a substance is being transferred from one phase to another phase at constant temperature and pressure (i.e at constt T & P), then there is no change in Gibb's free energy.

$$\text{Phase A} \rightleftharpoons \text{Phase B}$$

$G_A = G_B$

$\Rightarrow$ $dG_A = dG_B$ ... (i)

we know that,

$dG = VdP - SdT$

$dG_A = V_A dP - S_A dT$ ... (ii)

& $dG_B = V_B dP - S_B dT$ ... (iii)

Now making substitution from the equations (ii) & (iii) in (i), we get

$$V_A dP - S_A dT = V_B dP - S_B dT$$

$$\Rightarrow (S_B - S_A)dT = (V_B - V_A)dP \Rightarrow \boxed{\frac{dP}{dT} = \frac{S_B - S_A}{V_B - V_A}}$$

We have, $S_B - S_A = \Delta S = \frac{\Delta Q}{T}$ & $V_B - V_A = \Delta V$

Now making this substitution in equation (iv), we get

$$\frac{dP}{dT} = \frac{\Delta Q}{T}\frac{1}{\Delta V}; \frac{dP}{dT} = \frac{\Delta Q}{\Delta V}\frac{1}{T} \Rightarrow \boxed{\frac{dP}{dT} = \frac{\Delta H}{\Delta V}\left(\frac{1}{T}\right)}$$

This equation is known as 'Clausius Clapeyron Equation'.

Clausius-Clapeyron equation:

Clausius equation when applied to $L \rightleftharpoons V$ change is called clausius-clapeyron equation.

For one mole of an ideal gas in the process of vapourisation, we have

$$A(l) \xrightleftharpoons{\Delta H_v} A(g)$$

$\Delta H = \Delta H_v$, $\Delta V = V_g - V_l$

∴ (i) a

$$\frac{dP}{dT} = \frac{\Delta H_v}{(V_g - V_l)}\frac{1}{T} \quad \text{... (ii)}$$

But $V_g >> V_l$

∴ $V_g - V_l \approx V_g$

∴ (ii) ⇒

$$\frac{dP}{dT} = \frac{\Delta H_V}{V_g}\left(\frac{1}{T}\right) \qquad \text{... (iii)}$$

Now for one mol of an ideal gas, we know that $PV = RT;\ PV_g = RT;\ V_g = \frac{RT}{P}$

Now making this substitution in Equation (iii), we get

$$\frac{dP}{dT} = \frac{\Delta H_V}{\left(\frac{RT}{P}\right)} \times \left(\frac{1}{T}\right);\ \frac{dP}{dT} = \frac{\Delta H_V}{R}\frac{P}{T^2};\ \boxed{\frac{dP}{P} = \frac{\Delta H_V}{R}\frac{dT}{T^2}} \qquad \text{... (iv)}$$

Integrating both sides, we get

$$\int\frac{dP}{P} = \frac{\Delta H_V}{R}\int\frac{dT}{T^2}\,C;\ \boxed{\ln P = \frac{\Delta H_V}{R}\left(-\frac{1}{T}\right) + C} \qquad \text{... (v)}$$

$$\boxed{\log_{10} P = \frac{\Delta H_V}{2.303R}\left(-\frac{1}{T}\right) + C} \qquad \text{... (vi)}$$

Equations (v) & (vi) are known as Integrated form of clausius-clapeyron Eqns.

Eqns. (v) & (vi) can also be written as :

$$\ln P = \left(-\frac{\Delta H_V}{R}\right)\frac{1}{T} + C;\ y = mx + C \quad \text{OR} \quad \log_{10} P = \left(-\frac{\Delta H_V}{2.303R}\right)\frac{1}{T} + C;\ y = mx + C$$

Now Integrating Equation (iv) between the limits P_1 to P_2 and T_1 to T_2, we get

$$\int_{P_1}^{P_2}\frac{dP}{P} = \frac{\Delta H_V}{R}\int_{T_1}^{T_2}\frac{dT}{T^2};\ \ln\left(\frac{P_2}{P_1}\right) = \frac{\Delta H_V}{R}\left[-\frac{1}{T}\right]_{T_1}^{T_2};\ \ln\left(\frac{P_2}{P_1}\right) = \frac{\Delta H_V}{R}\left[-\frac{1}{T_2} + \frac{1}{T_1}\right]$$

$$\Rightarrow \quad \ln\left(\frac{P_2}{P_1}\right) = \frac{\Delta H_V}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$\Rightarrow \quad \boxed{\ln\left(\frac{P_2}{P_1}\right) = \frac{\Delta H_V}{R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)} \qquad \text{... (vii)}$$

OR

$$\boxed{\log_{10}\left(\frac{P_2}{P_1}\right) = \left(\frac{\Delta H_V}{2.303R}\right)\left(\frac{T_2 - T_1}{T_1 T_2}\right)} \qquad \text{... (viii)}$$

Equations (vii) & (viii) are also known as integrated form of clausius-clapeyron Equation.

Problem : Find the increase in the boiling point of water at 100°C when the pressure is increased by 1atm. Given, latent heat of vapourisation of steam = 540 cal/g & 1g of steam occupies a volume of 1677 C.C.

Soln : From clausius-clapeyron equation,

We have; $$\frac{dP}{dT} = \frac{\Delta H}{\Delta V}\left(\frac{1}{T}\right);\ \frac{dP}{dT} = \frac{\Delta H}{V_2 - V_1}\left(\frac{1}{T}\right) \qquad \text{......... (i)}$$

Here, $dP = 1\text{atm} = 1.01 \times 10^5\ \text{N/m}^2$ ... (ii)

$$\Delta H = 1\text{g} \times 540\frac{\text{cal}}{\text{g}} = 540 \times 4.18\text{J}$$

$\Rightarrow \quad \Delta H = 2257.2\text{J}$ ... (iii)

$V_1 = 1\text{C.C} = 10^{-6}\ \text{m}^3,\ V_2 = 1677\text{CC} = 1677 \times 10^{-6}\text{m}^3$

$\therefore \quad \Delta V = V_2 - V_1 = 1676 \times 10^{-6}\text{m}^3$ ... (iv)

$T = 100°\text{C} = 373\text{K}$ ... (v)

& $dT = ?$

Now making substitution from the equations (ii), (iii), (iv) & (v) in (1), we get

$$\frac{1.01\times10^{5}\,\text{N}/m^{2}}{dT} = \frac{2257.2\text{J}}{1676\times10^{-6}\,m^{3}} \times \frac{1}{373\text{K}}$$

$$\Rightarrow \quad dT = 1.01 \times 10^{5}\frac{\text{N}}{m^{2}} \times 1676 \times 10^{-6}\text{m}^{3} \times 373\text{K} \times \frac{1}{2257.2\text{J}}$$

$$\Rightarrow \quad dT = \frac{63139.948}{2257.2}\,\frac{(\text{N}-\text{m})}{\text{J}}\,\text{K} \quad \Rightarrow \quad dT = 27.97\text{K}$$

Problem: Calculate change in temp of boiling water when the pressure is increased by 27.12mm of Hg. The normal boiling point of water at 1atm is 100°C.

Given, Latent heat of steam = 537cal/g & specific volume of steam = 1674C.C

Soln : From clausius-clapeyron Equation, we have

$$\frac{dP}{dT} = \frac{\Delta H}{\Delta V}\left(\frac{1}{T}\right);\ \frac{dP}{dT} = \frac{\Delta H}{(V_2 - V_1)}\left(\frac{1}{T}\right)$$

$$\Rightarrow \quad dT = \frac{(V_2 - V_1)}{\Delta H} \times T \times dP \qquad \text{... (i)}$$

Here, $dP = 27.12\text{mm of Hg}$

$$\Rightarrow \quad dP = \frac{27.12}{760}\,\text{atm}\ [\because 1\text{atm} = 760\text{ mm of Hg}];\ dP = \frac{27.12}{760} \times 1.01 \times 10^{5}\text{N/m}^{2}$$

$$\Rightarrow \quad dP = 0.036041 \times 10^{5}\text{N/m}^{2} \qquad \text{... (ii)}$$

$$\Delta H = 1\text{g} \times 537\frac{\text{cal}}{\text{g}} = 537\text{cal} = 537 \times 4.18\text{J}$$

$$\Rightarrow \quad \Delta H = 2244.66\text{J} \qquad \text{... (iii)}$$

$$V_1 = 1.\text{C.C} = 10^{-6}\ \text{m}^3;\ V_2 = 1674\text{C.C} = 1674 \times 10^{-6}\ \text{m}^3$$

$$\Rightarrow \quad \Delta V = V_2 - V_1 = 1673 \times 10^{-6}\text{m}^3 \qquad \text{... (iv)}$$

$$T = 100°\text{C} = 373\text{K} \qquad \text{... (v)}$$

And $dT = ?$

Now making substitution from the equation (ii), (iii), (iv) & (v) in (1), we get

$$dT = \frac{1673\times10^{-6}\,m^{3}}{2244.66\text{J}} \times 373\text{K} \times 0.036041 \times 10^{5}\frac{\text{N}}{m^{2}}$$

$$\Rightarrow \quad dT = \frac{2249.0629}{2244.66}\,\frac{(N-m)}{J}K; \quad dT = 1K$$

Problem: When lead is melt at atmospheric pressure (The melting point is 600K), the density decreases from 11.01 to 10.65g/C.C & the latent heat of fusion is 24.5J/g. What is the melting point at a pressure of 100 atmosphere.

Soln : From clausius-clapeyron equation, we have

$$\frac{dP}{dT} = \frac{\Delta H}{\Delta V}\left(\frac{1}{T}\right); \quad \frac{dP}{dT} = \frac{\Delta H}{(V_2 - V_1)}\left(\frac{1}{T}\right)$$

$$\Rightarrow \quad dT = \frac{(V_2 - V_1)}{\Delta H} \times T \times dP \qquad \text{... (i)}$$

Here, $dP = (100 - 1)\text{atm} = 99\text{atm} = 99 \times 1.01 \times 10^5\ N/m^2$

$$\Rightarrow \quad dP = 99.99 \times 10^5 N/m^2 \qquad \text{... (ii)}$$

$$\Delta H = 1g \times \frac{24.5J}{g} = 24.5J \qquad \text{... (iii)}$$

$$V_1 = \frac{m_1}{d_1} = \frac{1gC.C}{11.01g} = \frac{1}{11.01}\times 10^{-6} m^3; \ V_1 = 0.0908265 \times 10^{-6} m^3$$

$$V_2 = \frac{m_2}{d_2} = \frac{1gC.C}{10.65g} = \frac{1}{10.65}\times 10^{-6} m^3$$

$$\therefore \quad \Delta V = V_2 - V_1 = (0.0938967 - 0.0908265) \times 10^{-6} m^3$$

$$\Delta V = 0.0030702 \times 10^{-6} m^3 \qquad \text{... (iv)}$$

$$T = 600K \qquad \text{... (v)}$$

And $dT = \frac{0.0030702 \times 10^{-6} m^3}{24.5J} \times 600K \times 99.99 \times 10^5 \frac{N}{m^2}$

$$\Rightarrow \quad dT = \frac{18.419358}{24.5}\,\frac{(N-m)}{J}K$$

$$\Rightarrow \quad dT = 0.7518105K$$

$\therefore$ Melting point at 100 atm = (600 + 0.7518105)K = 600.7518105K

Problem: At what pressure will ice melt at – 1°C assuming that ΔH_f is independent of pressure & $\Delta H_f = 6.0095$ KJ/ mol

Given $d_{H_2O} = 0.9998$ g/c.c and $d_{ice} = 0.9170$ g/c.c.

Soln: From clausius clapeyrom equation, we have

$$\frac{dP}{dT} = \frac{\Delta H}{\Delta V}\left(\frac{1}{T}\right) \qquad \text{...(i)}$$

$$\Rightarrow \quad \int_1^{P_2} dP = \frac{\Delta H_f}{\Delta V}\int_{T_1}^{T_2}\frac{dT}{T}$$

Here (i)

$$\Rightarrow \quad P_2 - 1\text{atm} = \frac{\Delta H_f}{\Delta V} \times 2.303 \log_{10}\left(\frac{T_2}{T_1}\right) \qquad \text{... (ii)}$$

Here

$\Delta H_f = 6.0095 \times 10^3$ J/mol ....(iii)

The molar mass of water= 18 g/mol

$= 18 \times 10^{-3}$ Kg/mol

$$V_1 = \frac{m_{ice}}{d_{ice}} = \frac{18\times10^{-3}\,kg.mol^{-1}}{\dfrac{0.9170\times10^{-3}\,kg}{10^{-6}\,m^2}} = \frac{18\times10^{-6}}{0.9170}\,m^3mol^{-1}$$

$$\Rightarrow \quad V_2 = \frac{m_{H_2O}}{d_{H_2O}} = \frac{18.10^{-3}\,kg.mol^{-1}}{\dfrac{0.9998\times10^{-3}\,kg}{10^{-6}\,m^3}} = \frac{18\times10^{-6}}{0.9998}\,m^3mol^{-1}$$

$\Rightarrow \quad V_2 = 18.00\,36001 \times 10^{-6}\ m^3mol^{-1}$

$\Rightarrow \quad \Delta V = V_2 - V_1 = (18.003601 - 19.629226)\times 10^{-6}\ m^3\ mol^{-1}$

$\Rightarrow \quad \Delta V = -1.625625 \times 10^{-6}\ m^3\ mol^{-1}$ ... (iv)

$T_1 = 0°C = 273K$

$T_2 = 1°C = 272K$

$$\log_{10}\left(\frac{T_2}{T_1}\right) = \log_{10}\left(\frac{272K}{273K}\right) = \log_{10}(0.996337)$$

$$\Rightarrow \quad \log_{10}\left(\frac{T_2}{T_1}\right) = -0.001593741 \qquad ...(v)$$

Now making substitution from the equation (iii), (iv) & (v) in (ii) we get

$$P_2 - 1atm = \frac{6.0095\times10^3\,Jmol^{-1}\times2.303\times[-0.001593741]}{-1.625625\,m^3mol^{-1}\times10^{-6}}$$

$$\Rightarrow \quad P_2 - atm = \frac{0.0220566\times10^9}{1.6225625}\frac{J}{m^3}$$

$$\Rightarrow \quad P_2 - 1atm = \frac{0.0135681\times10^9}{m^3}\times\frac{1}{1.01\times10^5}\,atm\,m^2 = \left[\begin{array}{ll} \therefore 1atm = 1.0\times10^5\,\dfrac{N}{m^2}\times\dfrac{m}{m} & \\ 1atm.m^3 & = 1.01\times10^5\,Nm \\ \Rightarrow 1atm.m^3 & = 1.01\times10^5\,J \end{array}\right]$$

$\Rightarrow \quad P_2 - 1\ atm = 0.0134338 \times 10^4$ atm

$\Rightarrow \quad P_2 = 1atm + 0.0134338 \times 10^4$ atm; $P_2 = 1$ atm $+ 134.338$ atm

$\Rightarrow \quad P_2 = 135.338$ atm

Effect of pressure on melting point:

For fusion

$$Solid \rightleftharpoons liquid$$

$$\because \quad \frac{dP}{dT} = \frac{\Delta H_f}{T_f(V_\ell - V_S)}$$

When a solid melt there may be increase in volume as in the case of certain substance like wax, & sulphur or there may be decrease in volume as in the case of certain substance like ice, Gallium & Bismuth.

$\Rightarrow \quad$ When $V_\ell > V_S$ e.g. wax, sulphur etc.

$$\frac{dP}{dT} = \frac{H_f}{T_f(V_\ell - V_S)}$$

$$(V_\ell - V_S) = +ve$$

$\therefore \quad \frac{dP}{dT} = +ve$

melting point of such substance rises with increase in pressure.

$\Rightarrow$ When $V_S > V_\ell$ e.g. ice, gallium, bismuth.

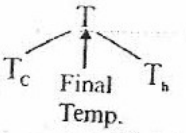
$$(V_\ell - V_S) = -ve$$

$\therefore \quad \frac{dP}{dT} = -ve$

melting point of such substances decreases with increase of pressure.

Entropy of mixing:

Two solid body of the same material each containing 1 mole of substance, one at higher temp. (T_h) and other at lower temperature (T_C). Both them be brought together. Heat will flow from hot body to the colder body.



If same substance and same amount

Heat lost by hot body = heat gained by cold body

$$-m\,C_P dT = m\,C_P dT\,;\ -(T - T_h) = (T - T_C)$$

$$T_h + T_C = 2T$$

Average temperature. $\boxed{T = \frac{T_h + T_C}{2}}$

$$\therefore \quad \Delta S_h = C_P \ell n \frac{T}{T_h}\,;\ \Delta S_C = C_P \ell n \frac{T}{T_C}$$

$$\therefore \quad \Delta S_{Total} = \Delta S_h + \Delta S_C$$

Entropy of mixing of ideal gas:

It is defined as the difference between the entropy of a mixture of the gas & the sum of entropies of seperate gases each at pressure 'P'.

Entropy of the mixture of gas depends on the partial pressure (P) exist in the mixture. So entropy

$$= \sum n_i (C_P \ell nT - R\ell np + S_0)$$

$$\therefore \quad \Delta S_{mix} = \sum n_i (C_P \ell nT - R\ell np + S_0) - \sum n_i (C_P \ell nT - R\ell nP + S_0)$$

$$\because \quad p = x_i P$$

$$\therefore \quad \Delta S_{mix} = \sum n_i (C_P \ell nT - R\ell n(x_i P) + S_0) - \sum n_i (C_P \ell nT - R\ell nP + S_0)$$

$$= \sum n_i (C_P \ell nT - R\ell nx_i - R\ell nP + S_0) + \sum n_i (-C_P \ell nT + R\ell nP - S_0)$$

$\boxed{\Delta S_{mix} = -\sum n_i (R\ell nx_i)}$ for 'n' mole.

For '1' mole

$$\text{molar entropy} = \frac{-R.\Sigma\, n_i \ell n\, x_i}{n} = -R\sum \frac{n_i}{n} \ell n\, x_i = \boxed{-R\Sigma x_i \ell in x_i}$$

Problem : 2 moles of N_2 are mixed with 3 moles of O_2. If they do not react, then calculate total change in entropy.

: We know that, $\Delta S_{mix} = -R\,\Sigma n_i \ln x_i$

$$\Rightarrow \quad \Delta S_{mix} = -R(n_1 \ln x_1 + n_2 \ln x_2);\ \Delta S_{mix} = -R\left[2mol \times \ln\left(\frac{2}{2+3}\right) + 3mol \times \ln\left(\frac{3}{2+3}\right)\right]$$

$$\Rightarrow \quad \Delta S_{mix} = -R\left[2\ln\left(\frac{2}{2+3}\right)+3\ln\left(\frac{3}{2+3}\right)\right]mol$$

$$\Rightarrow \quad \Delta S_{mix} = -R\left[2\ln\left(\frac{2}{5}\right)+3\ln\left(\frac{3}{5}\right)\right]mol$$

$$\Rightarrow \quad \Delta S_{mix} = -R[2\ln2 - 2\ln5 + 3\ln3 - 3\ln5]\text{mol}$$

$$\Rightarrow \quad \Delta S_{mix} = -R[2\ln2 + 3\ln3 - 5\ln5]\text{mol}$$

$$\Rightarrow \quad \Delta S_{mix} = -2.303\,R\left[2\log_{10}2 + 3\log_{10}3 - 5\log_{10}5\right]\text{mol}$$

$$\Rightarrow \quad \Delta S_{mix} = -2.303 \times 8.314\frac{\text{J}}{\text{K.mol}}[2\times0.3010 + 3\times0.4771 - 5\times0.6990]\text{mol}$$

$$\Rightarrow \quad \Delta S_{mix} = -19.15[0.6020 + 1.3313 - 3.4950]\text{J/K};\ \Delta S_{mix} = 29.90\ \text{J/K}$$

Problem: A piece of iron weighing 7.4 g is heated to 100°C and dropped into 100 g of water kept at 10°C. Calculate the final temperature of water, if no heat was lost to the surroundings. Take specific heats of iron and water as $0.499\,\text{Jg}^{-1}\text{K}^{-1}$ and $4.18\,\text{Jg}^{-1}\text{K}^{-1}$, respectively.

(a) 33°C (b) 16.5°C (c) 8.25°C (d) 4.125

Problem: The heat capacity of H_2O is $4.18\text{JK}^{-1}\text{g}^{-1}$ and chromium is $0.488\text{JK}^{-1}\text{g}^{-1}$. If 100 g of Cr at 100°C is added to a Styrofoam cup containing 50 g of water at 20°C, calculate the final temperature of the water. Assume that no heat is lost to the cup.

(a) 25.8°C (b) 38.5°C (c) 35.1°C (d) 47.9°C

Residual entropy:

There are certain solid which do not have perfect crystalline structure at 0°K like as H_2, D_2, CO, NO, N_2O & H_2O. So, they have certain amount of entropy even at absolute zero. This is called residual entropy.

If perfect crystalline, $S = k\ln w = k\ln 1^{NA} = k\times NA\ln 1 = 0$ (at 0°K, S = 0)

The cause of residual entropy is the confinement of molecules in the degenerate lowest energy level at 0°K in case of certain substance, i.e. crystals at 0°K are not perfect in true sense in such substances.

Residual entropy can be calculated by probability factor:

$$\boxed{S = k\ell nW} \qquad \text{where} \begin{bmatrix} W = \text{orientation of atom in the molecule} \\ = [\text{Arrangement}]^{N_A} \end{bmatrix}$$

⇒ At absolute zero

For CO = 2 arrangement

N_2O = 4 arrangement

ortho H_2 = 9 arrangement

Problem: Calculate residual entropy for CO.

Soln. $S = k\ell n[W]^{N_A} = N_A.k\ell n[W] = R\,\ell n\,2 = 8.317\times2.3036\times0.3010 = 5.76$ Joule.Kelvin^{-1}.mole^{-1}

Free energy functions:

In thermodynamics, two new functions have been introduced to explain various physical & chemical processes occuring at constant temperature & at constant pressure. These functions are called free energies or free energy functions. These are –

I – Helmholtz free energy / work function

II – Gibb's free energy/Gibb's potential.

Helmholtz's free energy or work function (A):

We know that, $dS \geq \frac{dq}{T}$; $dq = dU + PdV$

$$\therefore \quad dS \geq \frac{dU + PdV}{T}$$

$$TdS \geq dU + PdV$$

$$dU + PdV - TdS \leq 0$$

If volume is constant i.e. $dV = 0$

$$\therefore \quad (dU - TdS)_V \leq 0$$

If temp. of the system is also constant

$$\therefore \quad (\partial U - TS)_{V,T} \leq 0$$

The quantity $(U - TS)$ is referred to as Helmholtz free energy & is represented by A

$$\therefore \quad \boxed{A = U - TS} \qquad \text{... (1)}$$

Therefore, for a given process

$$(\partial A)_{V,T} \leq 0$$

⇒ A is a state function & hence dA is an exact differential.

⇒ A is an extensive property

⇒ Change in A for an isothermal process.

$$\because \quad A = U - TS$$

For initial state (1), $A_1 = U_1 - TS_1$

For final state (2), $A_2 = U_2 - TS_2$

$$\therefore \quad A_2 - A_1 = (U_2 - TS_2) - (U_1 - TS_1)$$

$$= (U_2 - U_1) - T(S_2 - S_1)$$

$$\boxed{\Delta A = \Delta U - T\Delta S} \qquad \text{... (2)}$$

Or for infinitesimal small change

$$\boxed{dA = dU - TdS} \qquad \text{... (3)}$$

Significance of A:

$$\because \quad A = E - TS$$

$$dA = dE - TdS \qquad \textbf{[at constant temperature]} \qquad \text{... (4)}$$

For a reversible process

$$dS = \frac{q_{rev}}{T} \qquad \left[2^{nd} \text{ law}\right] \qquad \text{... (5)}$$

$$q_{rev} = dU + W_{rev} \qquad \left[1^{st} \text{ law}\right] \qquad \text{... (6)}$$

From equation (4), (5) & (6)

$$dA = -W_{rev}$$

We know that work done in reversible process is maximum, hence

$$W_{rev} = W_{max} \quad \therefore \quad dA = -W_{max}$$

$$\boxed{-dA = W_{max}} \qquad [-dA = \text{decrease in work function}] \qquad \text{... (7)}$$

The equation (7) means that decreases in work function in an isothermal reversible process is equal to maximum work that can be obtained from the process.